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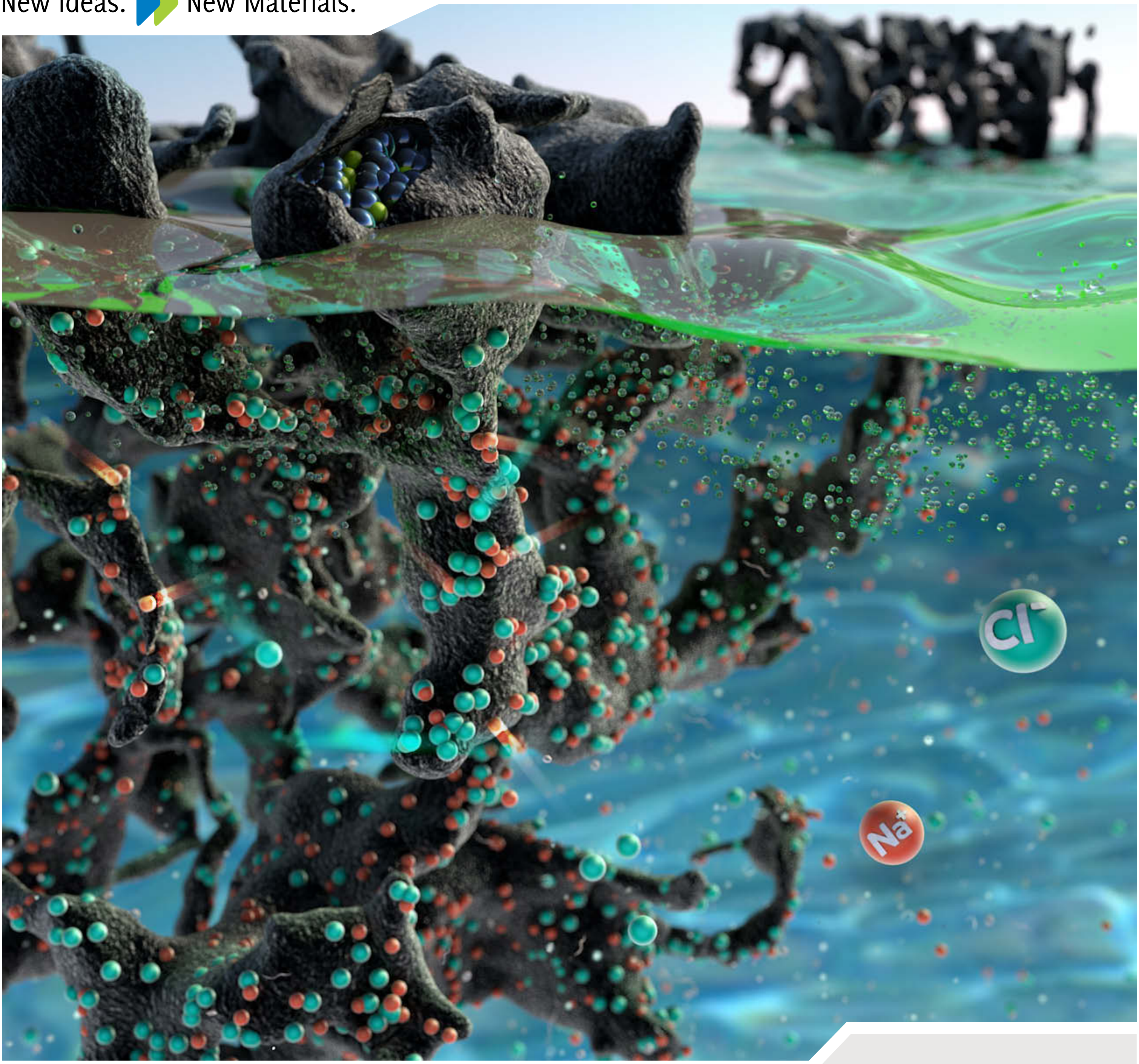

CDI&E 2015

INTERNATIONAL CONFERENCE ON CAPACITIVE DEIONIZATION AND ELECTROSORPTION

OCTOBER 26-29, 2015
SAARBRÜCKEN, GERMANY

INM
Leibniz Institute for New Materials

CDI&E 2015

International Conference on Capacitive Deionization and Electrosorption

organized by

INM – Leibniz Institute for New Materials

Saarbrücken, Germany, October 26-29, 2015

SCIENTIFIC ORGANIZATION: Volker Presser
INM – Leibniz Institute for New Materials, Saarbrücken
Department of Materials Science & Engineering , Saarland University

Matthew Suss
Technion – Israel Institute of Technology, Haifa

LOCAL ORGANIZATION: Christine Hartmann
Dominik Hell

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PROGRAM

MONDAY, OCTOBER 26, 2015

13:00 - 17:00		Tutorial
18:30 - 20:00		Welcome reception in Hotel Leidinger in downtown Saarbrücken (Mainzer Straße 10)

TUESDAY, OCTOBER 27, 2015

08:00		Registration
		OPENING WORDS
09:00		*Eduard Arzt* Scientific Director and Chairman, INM – Leibniz Institute for New Materials *Uwe Hartmann* Vice President for Planning and Strategy, Saarland University *Harald Schindel* Deputy Mayor of Saarbrücken *Volker Presser* Conference Chairman, Head of Energy Materials at INM
		SESSION 1 Basics and Perspectives Chair: Volker Presser
09:40	invited	“A Perspective on Recent Developments in Capacitive Deionization” *Matthew Suss*, Technion - Israel Institute of Technology, Haifa, Israel S. Porada, P. M. Biesheuvel, and V. Presser
10:10		“Pulse-Charged Capacitive Deionization: Increasing Effective Ion Mobility with Transient Fields” *Adam J. Rausch*, University of California, Berkeley (CA), United States of America A. J. Gadgil, and R. Kostecki
10:30		“Ion Electrosorption Studied by *in-operando* X-Ray Methods” *Christian Prehal*, Montanuniversität Leoben, Austria D. Weingarth, M. Burian, H. Amenitsch, V. Presser, and O. Paris
10:50		“Linking CDI Technology and Potential Controlled Chromatography Applications” *Ellen Biegert*, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany D. Hümmer, and M. Franzreb
11:10		Coffee break

SESSION 2
Flow-by CDI
Chair: Likun Pan

11:30 invited “Synthesis of Carbon Nanotube Electrodes and their Applications in Electrosorption”
Chongzheng Na, Texas Tech University, Lubbock (TX), United States of America

12:00 “Development and Application of Capacitive Deionization in Wastewater Treatment Plants”
Enrique García Quismondo, IMDEA Energy Institute, Madrid, Spain
C. Santos, R. Parrado, P. Lavela, C. Macías, L. C. de Pedro, and M. A. Anderson

12:20 “Modeling of Acid-Base Equilibria in CDI”
Jouke Dykstra, Wetsus, Leeuwarden / Wageningen University, The Netherlands
P. M. Biesheuvel, and A. van der Wal

12:40 “CDI Cell Electrodes and Architecture for Efficient Capacitive Desalination of Brackish Water”
Karthik Laxman, Water Research Center, Sultan Qaboos University, Al-Khoud, Sultanate of Oman
M. T. Zar Myint, and J. Dutta

13:00 Lunch break

SESSION 3
Hybrid and FCDI
Chair: Maarten Biesheuvel

14:00 invited “Hybrid Capacitive Deionization System and CDI Ragone Plot”
Jeyong Yoon, Seoul National University, Republic of Korea

14:30 “Continuous Membrane Capacitive Deionization Concepts Based on Flow Electrodes – From a Two to One Module Configuration”
Alexandra Rommerskirchen, RWTH Aachen University, Germany
Y. Gendel, and M. Wessling

14:50 “Flow-Through Electrode Capacitive Deionization Theory and Experiments”
Eric Guyes, Technion - Israel Institute of Technology, Haifa, Israel
A. N. Shocron, P. M. Biesheuvel, and M. E. Suss

15:10 “Fabrication and Characterization of Activated Carbon@Ion-Conducting Polymer for Well-Dispersed Flow Electrodes in FCDI System”
Hong-Ran Park, Korea Institute of Energy Research, Daejeon, Republic of Korea
J. Choi, S. Yang, J. Yeo, M. Han, and D. K. Kim

15:30 “Plug Flow Desalination”
Susan H. Roelofs, University of Twente, Enschede, The Netherlands
A. van den Berg, and M. Odijk

15:50 Coffee break

		SESSION 4 Faradaic CDI Chair: Matthew Suss
16:10	invited	“Theoretical Modeling of Mixed Capacitive-Faradaic Processes in CDI” *Maarten Biesheuvel*, Wetsus, Leeuwarden / Wageningen University, The Netherlands
16:40		“Pseudocapacitive Deionization: Redox-Mediated Electrosorption of Anions” *Xiao Su*, Massachusetts Institute of Technology, Cambridge (MA), United States of America T. A. Hatton
17:00		“Potential of Zero Charge Modified Carbon Electrodes for CDI and MCDI Applications” *Ayokunle Omosebi*, University of Kentucky, Lexington (KY), United States of America X. Gao, J. Landon, and K. Liu
17:20		“Hybrid Capacitive Deionization System with Sodium Iron Pyrophosphate” *SeongHwan Kim*, Seoul National University, Republic of Korea J. Lee, and J. Yoon
17:40		“Hybrid Electrochemical Interfaces for Control over Separation and Catalytic Processes” *Xianwen Mao*, Massachusetts Institute of Technology, Cambridge (MA), United States of America W. Tian, G. C. Rutledge, and T. A. Hatton
18:00 - 19:30		Poster session

WEDNESDAY, OCTOBER 28, 2015

		SESSION 5 Special Ion Removal Chair: Linda Zou
09:20	invited	“Electrosorption Technology for Heavy Metal Removal from Waste Water” *Xiaowei Sun*, EST Water & Technology Co., Ltd., Changzhou, China
09:50		“Batch and Single Pass Studies of Fluoride and Nitrate Removal from Brackish Groundwaters by Capacitive Deionization” *Peter Kovalsky*, University of New South Wales, Kensington, Australia W. Tang, D. He, and T. D. Waite
10:10		“Investigation of Removal of Heavy Metals from Aqueous Solutions by Capacitive Deionization” *Nung Lee*, National Taiwan University, Taipei, Taiwan C. Hou
10:30		Coffee break

SESSION 6
Energy Harvesting
Chair: Xiaowei Sun

10:50	invited	“Application of the Electrosorption Process for Energy Generation” *Bert Hamelers*, Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands
11:20		“New Low-Cost Heat-to-Current Converters Can Be Built from Conventional Supercapacitors” *Andreas Härtel*, Johannes Gutenberg University Mainz, Germany M. Janssen, D. Weingarth, V. Presser, and R. van Roij
11:40		“Calorimetry of Electric Double Layer Formation at CDI Electrodes” *Ben H. Erné*, Utrecht University, The Netherlands E. Griffioen
12:00		“Effect of Electrode Material Selection on the Energy Production by Double Layer Expansion” *Guillermo Iglesias Salto*, University of Granada, Spain M. M. Fernández, S. Ahualli, M. L. Jiménez, and A. V. Delgado
12:20		“A Novel Variable Capacitance Engine Using Periodically Squeezed Liquid Bridges” *Mathijs Janssen*, Utrecht University, The Netherlands B. Werkhoven, and R. van Roij
12:40		Lunch break

SESSION 7
Ion Processes
Chair: Chongzheng Na

13:40	invited	“Selective Removal of Specific Ions in Capacitive Deionization” *Jae-Hwan Choi*, Kongju National University, Cheonan, Republic of Korea
14:10		“Effects of Surface Transport on Water Desalination by Capacitive Deionization” *Amit Shocron*, Technion – Israel Institute of Technology, Haifa, Israel M. Suss
14:30		“Multi-Ionic Effects on the Capacitance of Porous Carbon Electrodes” *María L. Jiménez Olivares*, University of Granada, Spain M. M. Fernández, S. Ahualli, and A. V. Delgado
14:50		“CDI Controlled Spectral Emission” *Karni Wolowelsky*, Technion - Israel Institute of Technology, Haifa, Israel M. Bercovici, and C. Rotschild
15:10		Coffee break

SESSION 8
Heteroatom Carbons and beyond
Chair: Jae-Hwan Choi

15:30 invited “Enhanced Capacitive Deionization Ability of Nanocarbon Materials by Nitrogen Doping”
Likun Pan, Engineering Research Center for Nanophotonics and Advanced Instrument, East China Normal University, Shanghai, China
Y. Liu, X. Xu, M. Wang, and T. Lu

16:00 “Capacitive Deionization Using Biomass-Based Microporous Salt-Templated Heteroatom-Doped Carbons”
Sławomir Porada, INM – Leibniz Institute for New Materials, Saarbrücken, Germany
F. Schipper, M. Aslan, M. Antonietti, V. Presser, and T. P. Fellinger

16:20 “Nitrogen-Doped Carbon Aerogels for Capacitive Deionization”
Qinghan Meng, Beijing University of Chemical Technology, China
Y. Wei, and B. Cao

16:40 “Pseudocapacitive Electrosorption of Carbon Dioxide and Other Acid Gases”
Alan Hatton, Massachusetts Institute of Technology, Cambridge (MA), United States of America
S. Voskian

17:00 Bus transfer to social events in Völklingen:
18:00 World Heritage Site Völklingen Ironworks
19:30 Conference Dinner in “Platform 11 ¾”
~21:30 Return to Saarbrücken (main hotels and Aula)

THURSDAY, OCTOBER 29, 2015

SESSION 9
MCDI
Chair: Bert Hamelers

09:00 invited “Ion Transport Through Ion Exchange Membranes”
Matthias Wessling, DWI - Leibniz Institute for Interactive Materials / RWTH Aachen, Germany

09:30 “Modeling Ion-Exchange Membrane Transport for Energy Harvesting and Desalination”
Michele Tedesco, Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands
H. V. M. Hamelers, and P. M. Biesheuvel

09:50 “Quantitative Analysis of Mechanisms of Ion-Exchange Resin-Coated Capacitive Deionization”
Kyusik Jo, Seoul National University, Republic of Korea
S. P. Hong, and J. Yoon

10:10		"Advanced Full Scale Membrane Capacitive Deionization System for River Water Treatment" *Piotr Dlugolecki*, Voltea B.V., Sassenheim, The Netherlands M. Poos, A. Crowell, and B. Brister
10:30		"Asymmetric Membrane Capacitive Deionization with Eco-Friendly Cation Exchange Media Coated-Carbon Electrode for Hardness Control" *Jiho Lee*, Seoul National University, Republic of Korea H. Yoon, and J. Yoon
10:50		Coffee break
		SESSION 10 MCDI Chair: Volker Presser
11:10	invited	"Research on Electrodes and Ion Exchange Membranes in Capacitive Deionization" *Linda Zou*, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates
11:40		"Ion Exchange Spacer Materials for Enhanced Desalination Rate and Charge Efficiency in Capacitive Deionization" *Dennis Cardoen*, VITO, Mol, Belgium S. de Peuter, J. Helsen, and R. Zhao
12:00		"Capacitive Separators for Enhanced Desalination Performance of Membrane Capacitive Deionization" *Yanhong Bian*, Tsinghua University, Beijing, China P. Liang, Y. Jiang, C. Zhang, and X. Huang
12:20		"A New Continuous Method to Desalinate Salt Water" *Gijs J. Doornbusch*, Technion – Israel Institute of Technology, Haifa, Israel J. E. Dykstra, P. M. Biesheuvel, and M. E. Suss
12:40		Concluding remarks
13:00		Lunch break
14:00		Guided lab tour through the INM – Leibniz Institute for New Materials (registration on site)

ORAL PRESENTATIONS

SESSION 1: BASICS AND PERSPECTIVES

O1-1 (invited)

A PERSPECTIVE ON RECENT DEVELOPMENTS IN CAPACITIVE DEIONIZATION

Matthew E. Suss[1], S. Porada[2], P.M. Biesheuvel[3,4], and V. Presser[2,5]

[1] Mechanical Engineering, Technion - Israel Institute of Technology, Haifa, Israel, 32000

[2] INM - Leibniz Institute for New Materials, 66123 Saarbrücken, Germany

[3] Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands

[4] Laboratory of Physical Chemistry and Soft Matter, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

[5] Department of Materials Science and Engineering, Saarland University, Campus D2 2, 66123 Saarbrücken, Germany

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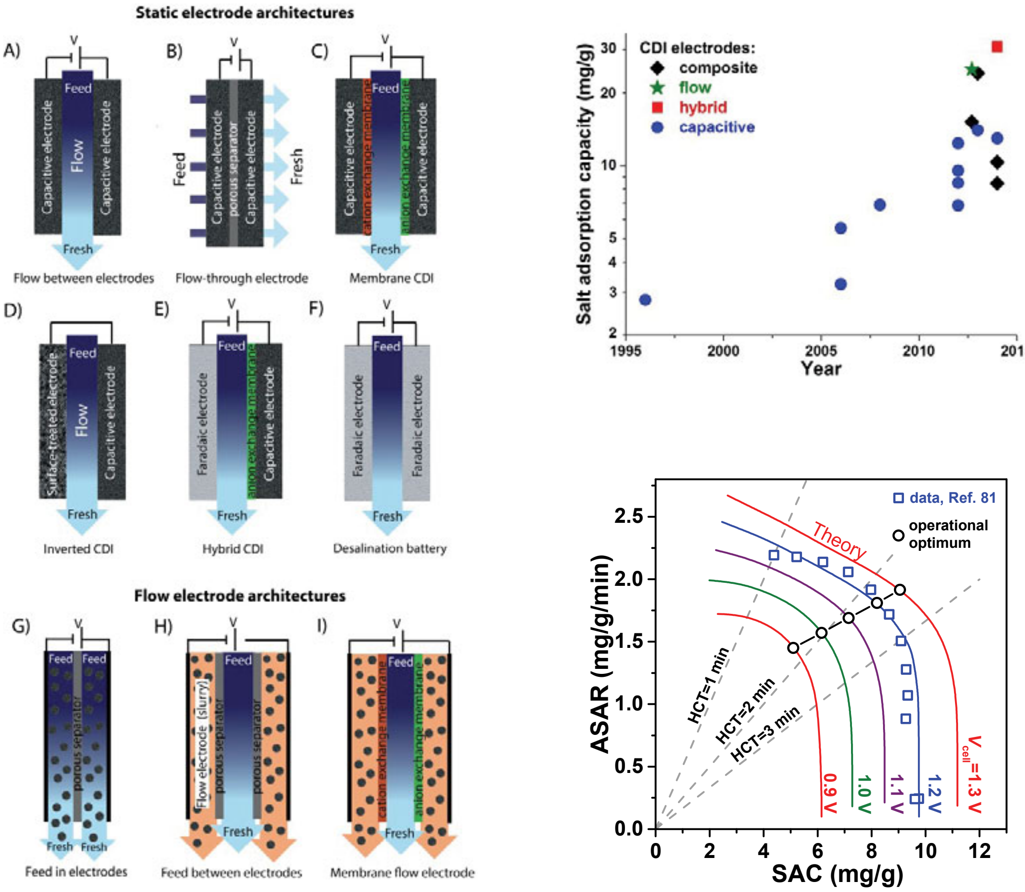

Fig 1: left) Schematics of classic and recent CDI cell architectures. top-right) Historical evolution of the salt storage capacity of CDI electrodes. top-left) A Kim-Yoon plot for representing CDI cell performance.

Capacitive deionization (CDI) is a fast-emerging technology which is most commonly applied to the desalination of brackish feedwaters. A traditional CDI cell consists of two static film porous carbon electrodes separated by a feed channel (a porous dielectric layer or open channel). The past decade, and in particular the past three years, has seen the emergence of numerous novel cell architectures, electrode materials, applications, experimental methods, and theoretical advances, completely revolutionizing this field.[1] We will highlight the most promising recent developments, propose the standardization of CDI performance metrics, and also discuss possible future research directions for this growing field.

Reference:

1. ME Suss, S Porada, X Sun, PM Biesheuvel, J Yoon, and V Presser. "Water desalination via capacitive deionization: what is it and what can we expect from it?" Energy & Environmental Science (2015), http://dx.doi.org/10.1039/C5EE00519A, (Open Access).

O1-2

PULSE-CHARGED CAPACITIVE DEIONIZATION: INCREASING EFFECTIVE ION MOBILITY WITH TRANSIENT FIELDS

Adam J. Rausch[1], Ashok J. Gadgil[1,2], and Robert Kostecki[2]

[1] Civil and Environmental Engineering, University of California, Berkeley, U.S.A.

[2] Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, U.S.A.

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2.5 billion people rely solely on groundwater for basic needs,[1] but an estimated 20% of aquifers are being tapped unsustainably.[2] In addition, remaining freshwater sources face salinization threats from seawater intrusion, agricultural practices, and industrial contamination. The result is an estimated 1.1 billion people living in places with brackish ground water,[3] and communities increasingly dependent on these brackish sources for drinking water. Drinking this water causes great suffering.

As with many such problems, this dependence disproportionately affects the poorest among us. For example, 60% of India's fresh groundwater resources are expected to be depleted within 20 years.[4] And while mature technologies for removing these salts exist, costs and infrastructure requirements often make these solutions impractical in rural developing settings.

Capacitive deionization (CDI) offers particular promise for low-cost, off-grid treatment of brackish groundwater, due to low energy requirements at typical influent concentrations (1000-3500 ppm).[5] It is also well-matched for intermittent, off-grid power sources. Unfortunately, traditional CDI can also be slow, which presents a challenge for application at scale, especially in developing settings. The traditional configuration relies on electrically-induced ion flow across a (typically mm-scale) channel, which is initially rapid, but slows as electrical double-layers form at the electrodes. To address this, one approach pumps the water through thick electrodes built with µm-scale pathways.[6] Another method adds carbon beads that become charged within the channel, adsorb ions, and can later be separated mechanically.[7] Both methods reduce the distance necessary for ions to travel prior to adsorption, but increase required pressure, and hence energy requirements.

It appears possible, however, to operate CDI in an altogether different way. In our arrangement, the electrodes are not held at a constant voltage with the resultant slow, steady transfer of charge. Instead, the cell is charged in discrete steps, transferred to the electrodes by periodic, short-duration, high-voltage pulses. Each pulse creates a transient voltage spike. The rise is induced by the high-voltage pulser, but the fall is due to the response of the double layers within the cell. Instead of seeing one brief high-magnitude field, ions in the channel see periodic high-magnitude fields and react to each pulse. Redox reactions are still avoided, so long as each spike is shorter than the timescales over which redox reactions are induced.

Though the high-magnitude fields are present for only a fraction of the duty cycle, they are many orders of magnitude higher than those in the bulk after double-layers have been established. Thus, this arrangement induces higher effective ion mobility, a nonlinear current response to applied voltage, and hence an opportunity to improve performance at only modest energy cost.

Our presentation will discuss early theoretical formulations, modeling efforts, and requisite characterizations for pulse-charged CDI.

References:

1. *UN World Water Development Report 2015;* UNESCO: Paris, **2015**.

2. Gleeson, T.; Wada, Y.; Bierkens, M. F. P.; van Beek, L. P. H. Water balance of global aquifers revealed by groundwater footprint. *Nature* **2012**, 488: 197-200.

3. van Weert, F.; van der Gun, J.; Reckman, J.; *Global Overview of Saline Groundwater Occurrence and Genesis;* IGRAC: Utrect, **2009**.

4. *Deep Wells and Prudence: Towards Pragmatic Action for Addressing Groundwater Overexploitation in India;* World Bank: Washington, D.C., **2010.**

5. Oren, Y. Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review). *Desalination* **2008**, 228 10-29.

6. Suss, M. E.; Baumann, T. F.; Bourcier, W. L.; Spadaccini, C. M.: Rose, K. A.; Santiago, J. G.; Stadermann, M. Capacitive desalination with flow-through electrodes. *Energy and Environmental Science* **2012**, 5, 9511-9519.

7. Hatzell, K. B.; Owama, E.; Ferris, A.; Daffos, B.; Urita, K.; Tzedakis, T.; Chauvet, F.; Taberna, P.; Gogotsi, Y.; Simon, P. Capacitive deionizaiton concept based on suspension electrodes without ion exchange membranes. *Electrochemistry Communications* **2014**, 43, 18-21.

O1-3

ION ELECTROSORPTION STUDIED BY IN-OPERANDO X-RAY METHODS

Christian Prehal[1], Daniel Weingarth[2], Max Burian[3], Heinz Amenitsch[3], Volker Presser[2,4], and Oskar Paris[1]

[1] Institute of Physics, Montanuniversitaet Leoben, Leoben, Austria

[2] INM – Leibniz Institute for New Materials, Saarbrücken, Germany

[3] Institute of Inorganic Chemistry, Graz University of Technology, Graz, Austria

[4] Department of Materials Science and Engineering, Saarland University, Saarbrücken, Germany

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A fundamental understanding of the electrosorption of ions in carbon nanopores is essential for improving the performance of technologies like capacitive de-ionization (CDI) or energy storage in electrical double-layer capacitors (EDLCs). In both cases ions rearrange within the nanopores of a carbon electrode as a response of an applied voltage. The exact mechanism how the ions counterbalance the electrode charge is so far not fully understood. Simulations have predicted a transition from pure ion exchange to preferred counter-ion adsorption as the ionic strength and the applied charge is increased.[1] Experimentally, this information is difficult to achieve, and comprehensive *in-situ* characterization techniques which are sensitive to ion concentration changes within the pores are required. Since conventional electrochemical methods are only sensitive to the total charge, the behaviour of ions can only be studied in an indirect way with limited information.

We employed for the first time *in-situ* X-ray transmission (XRT) and *in-situ* small-angle X-ray scattering (SAXS) during charging and discharging of an *in-operando* supercapacitor cell using aqueous electrolytes within different nanoporous carbons as electrode material. XRT measurements are directly sensitive to the sum of the cation and anion concentration within the working electrode weighted by their X-ray absorption coefficient. Together with the simultaneously measured electrical current signal, the cation and anion concentration changes can be separated. For 1M aqueous electrolyte solutions (CsCl, KCl, NaCl), ions were found to compensate the applied electrode charge by pure ion exchange over a large potential window, while the total ion concentration (cations + anions) within the electrode remains constant (see Fig. 1). Besides this important information about the global ion flux additional structural information was derived from the *in-situ* SAXS measurements. In addition to the global ion concentration changes, ions are found to rearrange across the nanopores as a response of an applied voltage.[2] In particular, it was found that locally counter-ions move preferably from the center towards the pore walls as soon as a voltage is applied.

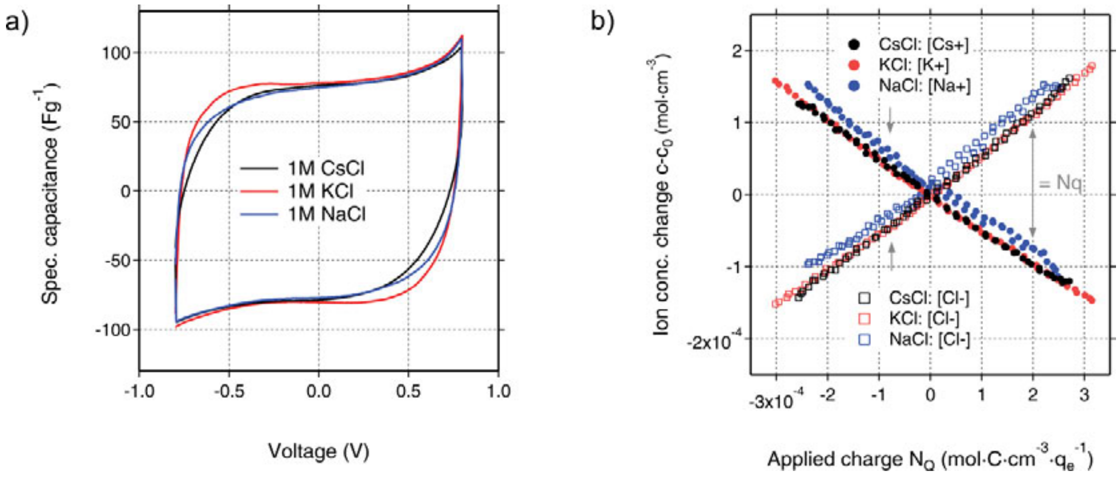

Fig. 1: In a) the cyclic voltammetry (CV) curves for the *in-operando* supercapacitor cells using an activated carbon electrode with a 1M aqueous CsCl, KCl and NaCl electrolyte are shown. In b) the cation and anion concentration changes for the three electrolytes as a function of the applied electrode charge is given. The data shown here was published in a similar form in Ref. 2.

References:

1. P. M. Biesheuvel, S. Porada, M. Levi and M. Z. Bazant, *J. Solid State Electr.*, 2014, 18, 1365-1376.
2. C. Prehal, D. Weingarth, E. Perre, R. T. Lechner, H. Amenitsch, O. Paris and V. Presser, *Energy Environ Sci*, 2015, 8, 1725-1735.

O1-4

LINKING CDI TECHNOLOGY AND POTENTIAL CONTROLLED CHROMATOGRAPHY APPLICATIONS

Ellen Biegert, Dominik Hümmer, and Matthias Franzreb

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Looking at process schemes for the purification of biopharmaceutical products, it shows that chromatography is a widely applied and effective unit operation. However, conventional chromatography using large volumes of equilibration, washing and elution buffers is an expensive and often non-sustainable process. In consequence, there is a strong need for more economic and sustainable sorption processes in biotechnology.[1]

An interesting alternative to conventional chromatography is the so-called potential controlled liquid chromatography (PCC) method, which applies a switchable electric potential to a conductive porous stationary phase in order to control the ad- and desorption of ionic biomolecules. This method requires neither a specific elution nor any equilibration buffer and is therefore predestinated for continuous operation modes.

However, previously used conductive stationary phases for PCC often had relatively small specific surface areas and consequently low capacities. In our study we screened highly porous carbon materials for they suitability for PCC applications by first determining their electrical capacities via cyclovoltammetry (CV) and chronoamperometry (CA) measurements. Their study showed that materials regularly used in CDI applications are also promising candidates for improved PCC, since both techniques are based on the same physical principle although using different ways of operation. So we henceforth oriented our column design on the use of CDI materials. We developed a 3D-printed flow cell that allows a three-electrode-setup and precise voltage supply to the adsorption area and connected it to an HPLC system. Using crotonic acid as a model substance for industrially relevant small biomolecules, we achieved a capacity of 4.8 mg crotonic acid per g of electrode material, which is approximately ten times higher than conventional PCC systems applying glassy carbon as electrode material.

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[1] http://www.bio-pro.de/magazin/thema/04132/index.html?lang=de, 15.06.2015.

SESSION 2: FLOW-BY CDI

O2-1 (invited)

SYNTHESIS OF CARBON NANOTUBE ELECTRODES AND THEIR APPLICATIONS IN ELECTROSORPTION

Chongzheng Na

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Carbon nanotubes (CNTs) made of concentric rolls of graphene sheets often have diameters on the order of nanometres but can grow up to centimetres in length. The quasi-one-dimensional structure gives CNTs remarkable electrical conductivity, excellent tensile strength, and a high surface-to-volume ratio, making them superb anisotropic materials for manufacturing electrodes to remove ions from water through electrosorption. To maximize the electrochemical surface area of a CNT electrode, a large number of CNTs are often used together and aligned along their longitudinal directions, forming CNT arrays. This talk introduces the basic steps for synthesizing CNT electrodes using chemical vapour deposition (CVD), one of the standard methods for large-scale CNT production. Detailed discussion will be given to the importance of creating buffer layers on complex supporting substrates using several methods developed by us in the past few years, including layer-by-layer assembly, chemical bath deposition, and passivation layer etching. The performance and optimization of CNT electrodes will be demonstrated through the simultaneous reduction and removal of hexavalent chromium, providing positive correlation between CNT length with electrochemical surface area.

O2-2

DEVELOPMENT AND APPLICATION OF CAPACITIVE DEIONIZATION IN WASTEWATER TREATMENT PLANTS

Enrique García-Quismondo[1], Cleis Santos[1], Rita Parrado[2], Pedro Lavela[3], Carlos Macías[4], Luis Carlos De Pedro[5], and Marc A. Anderson[1,6]

[1] Electrochemical Processes Unit, IMDEA Energy, 28935 Móstoles, Spain

[2] R&D Department, Proyectos de Ingeniería y Gestión, S.A. (PROINGESA), P: I. San Cristobal, 47012 Valladolid, Spain

[3] Laboratorio de Química Inorgánica, Universidad de Córdoba, Campus de Rabanales, 14071 Córdoba, Spain

[4] Nanoquimia S.L., P.L La Minilla, La Rambla, 14540 Córdoba, Spain

[5] Isolux Ingeniería, S.A., C/ Caballero Andante 8, 28021 Madrid, Spain

[6] Environmental Chemistry & Technology Program, University of Wisconsin, Madison, WI 53706, USA

Electricity consumption in wastewater reuse and desalination processes is an increasing concern of the water treatment industry. As a result, utilities have been in search of process and technologies that could lower power consumption in these processes. As consequence, the implementation of technologies such as reverse osmosis or electrodialysis to remove ionic components of wastewater and brackish water has been of interest. However, with these existing technologies the cost of water production is still high and finding new techniques to enable further progress in reducing power consumption is of great value [1–3].

In this study, within the framework of ADECAR project, formed by a consortium of three companies, a university and a research center, with the financial support of the Ministry of Economy and Competitiveness (IPT-2011-1450-310000 (ADECAR project), we have evaluated the economic impact of applying the Capacitive deionization (CDI) technology to the regeneration of wastewater to efficiently eliminate dissolved nutrients, in particular ionic species containing nitrogen, phosphorus and sulphates. In this respect our project has addressed the following aspects:

- In a conventional wastewater treatment plant (WWTP) different streams were identified as being more suitable for employing capacitive deionization.
- New electrodes were prepared based on two types of carbonaceous materials: active carbon powder and carbon aerogels [4].
- Two reactors were designed which were adapted to the characteristics of each electrode type.

In a second part of the project, we designed and manufactured a CDI prototype with 300 cm^2 electrodes and 20 cells. The prototype was tested on brackish waters (3 000 mg/L) and water treatment efficiency results were first compared to results obtained in the laboratory scale cell. Secondly, a test conducted on brackish water was used to estimate CDI treatment costs in a full-scale industrial unit and to simulate its integration in a WWTP. In order to determine if the technology has the potential to be competitive, a simulation study employing the main waste water streams of the process was performed. This simulation model examined flow rates, ionic composition and energy consumption. Finally, capital cost projections for using CDI in WWTP were done assuming the integration of the technology in streams where the balance between cost and the removal of ions were optimal, for example, after the Biological Secondary treatment or in Tertiary treatment.

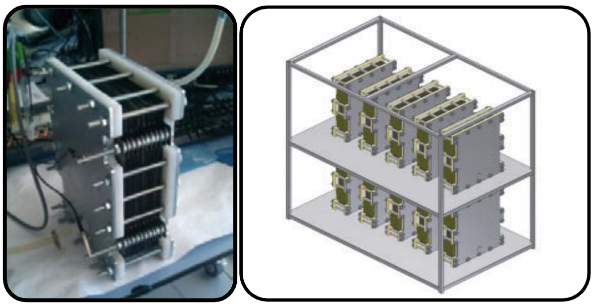

Figure 1. (Left) CDI Laboratory Reactor (Right) Full-scale industrial CDI unit (schematic view).

Results have shown that CDI integration into a WWTP is technically feasible and could allow efficient removal of dissolved ions making the plant more manageable. Moreover, CDI implementation would reduce the content of dissolved contaminants in the liquid waste in those cases where a transitory effects or a concentration peak of toxic elements, in particular ionic species containing nitrogen, phosphorus, sulphates, boron, lithium or arsenic occurs.

References:

[1] M. a. Anderson, A.L. Cudero, J. Palma, Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete?, Electrochimica Acta. 55 (2010) 3845–3856.

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O2-3

MODELING OF ACID-BASE EQUILIBRIA IN CDI

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Capacitive Deionization adsorbs salt from the water into Electrical Double Layers (EDLs) formed within carbon micropores. During the adsorption phase of a CDI cycle, ions are adsorbed from the spacer channel through which the water flows into porous carbon electrodes. In these electrodes, we distinguish two different types of pores. Firstly, the micropores, where EDLs are formed and consequently ions are stored near the charged carbon interfaces. Secondly, we model the macropores, through which the salt is transported to the micropores, subject to diffusional and migrational forces.

The micropores have a pore size of the order of 2 nm or less. For an NaCl solution of 10 mM, the Debye length is approximately 3 nm at 20 ºC, which means that the EDL thickness is about 6-10 nm. As the pore size is smaller than the EDL thickness, EDLs are strongly overlapping and the commonly used Gouy-Chapman-Stern theory to describe these EDLs is not valid. Therefore, we make use of another theory, the modified Donnan (mD) model, which has shown to describe the salt adsorption in porous carbon electrodes very well for CDI [1,2,3].

To compute the salt adsorption in the electrodes dynamically, we model the transport of salt through the macropores. This transport typically occurs on a length scale of 100s of micrometers. Combining transport and EDL formation in one theory implies combining processes on two vastly different length scales. A second complication in modeling is that the local adsorption of salt from the macropores into the EDLs is much faster than the transport of the salt across the electrode, which requires methods to couple the mD model to a dynamic transport model.

Besides the adsorption of salt, also protons and hydroxyl ions are adsorbed in the micropores. To include this process in our model, we have to model the transport of more than two ionic species and include the acid-base equilibrium reactions between protons and hydroxyl ions. To simplify the model, we assume these reactions to be infinitely fast. Therefore, we can eliminate the reaction kinetics from the model, and instead, implement the acid-base equilibrium conditions in our model.

We show how we can couple EDL formation, ion transport and acid-base equilibria modeling in CDI to improve our understanding of the dynamic salt adsorption process, as well as the resulting pH fluctuations of the effluent of the CDI cell.

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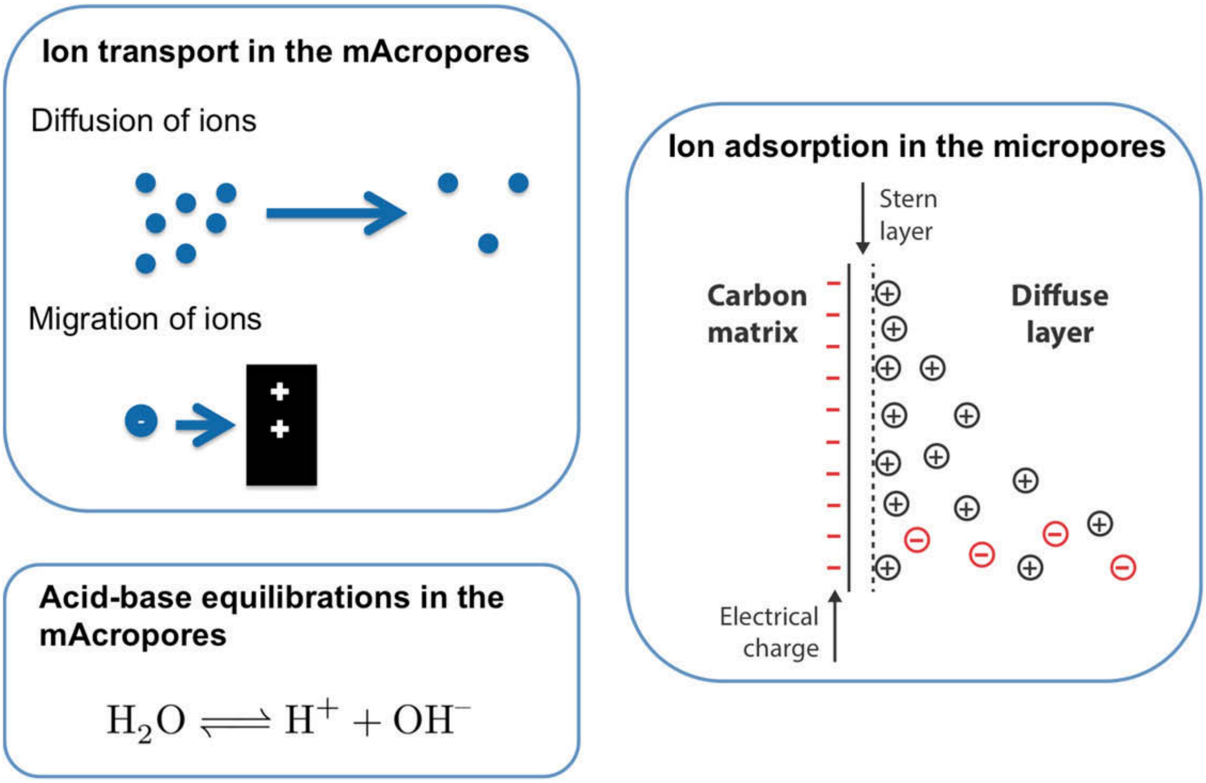

Figure 1. Coupling ion adsorption modeling in the micropores of porous carbon electrodes to ion transport and acid-base equilibrations in the mAcropores.

O2-4

CDI CELL ELECTRODES AND ARCHITECTURE FOR EFFICIENT CAPACITIVE DESALINATION OF BRACKISH WATER

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Capacitive deionization works on the principle of electric field mediated ion adsorption in electrical double layers at electrode surfaces. The extent of ion adsorption is observed to be a function of field distribution, electrode symmetry and capacitance of the cell electrodes. It is thus important to optimize these parameters for efficient salt adsorption on the electrodes and improve the charge efficiency of the CDI cell.

In this work we explore techniques to improve the electric field distribution and strength without increasing the applied potential and show an improvement in the salt adsorption capacity along with a reduction in the total power consumption. It was also observed that symmetry between the cell electrodes plays a key role in optimizing the adsorption capacity. The symmetry was observed to be independent of the surface area of the electrodes and governed primarily by the specific capacitance of the electrodes. We have explored the effect of the polarity of applied potential on the selective removal of ions and introduce a new CDI cell architecture which can substantially increase the salt adsorption and charge efficiency of the cell, while further reducing the power consumption. The design of a larger prototype will also be discussed and results of its usage for ground water desalination will be presented. The results indicate that a CDI cell works as both a desalination unit and a disinfection unit for ground water purification.[1-4]

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O3-1 (invited)

HYBRID CAPACITIVE DEIONIZATION SYSTEM AND CDI RAGONE PLOT

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Based on a porous carbon electrode, capacitive deionization (CDI) is a promising desalination technology in which ions are harvested and stored in an electrical double layer. This technology has various advantages such as simple operation, energy efficient and environment-friendly process. However, the deionization capacity and rate of CDI systems is not sufficient for desalting saline water. In this talk, we present a hybrid CDI with superior performances and an advance CDI system evaluation method called CDI Ragone plot.

Firstly, we present a novel desalination technique referred to as “hybrid capacitive deionization (HCDI)”, which combines CDI with a sodium battery system. HCDI consists of a sodium manganese oxide (Na4Mn9O18) electrode, an anion exchange membrane and a porous carbon electrode. In this system, sodium ions are intercalated in the Na4Mn9O18 electrode, whereas chloride ions are adsorbed on the surface of the activated carbon electrode during the desalination process. The deionization capacity of HCDI (31.2 mg g^{-1}) was more than two times than that of CDI system (13.5 mg g^{-1}). Also, HCDI system performed a rapid ion removal rate and excellent stability. Thus, HCDI system could be a feasible method for desalting a more saline sodium chloride solution in capacitive techniques.

Secondly, we propose the CDI Ragone plot, which is a novel concept to evaluate CDI performance. It was developed to show deionization capacity and rate over wide range of current load in constant current operation, thus maximum capacity and rate could be found. It allows intuitive acquisition of deionization performance obtained in various parameters such as flow rate, thickness and concentration of the feed solution. In conclusion, it provides an insight to understand deionization capacity and rate of the CDI system. Therefore, it would be a comprehensive guide for deionization performance as a future standard in CDI.

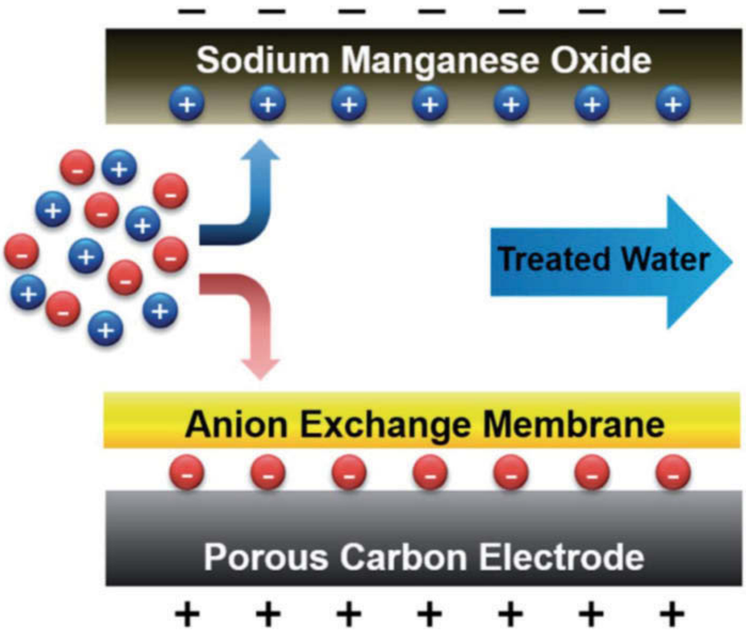

Figure 1. Schematic diagram of desalination via HCDI

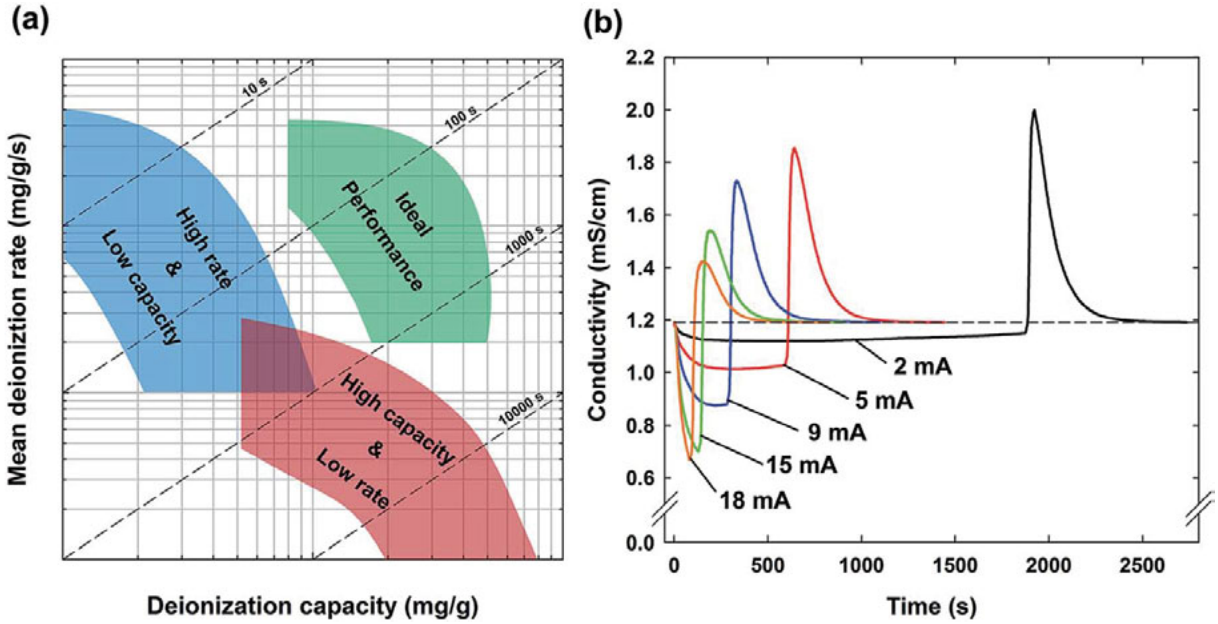

Figure 2. A conceptual diagram of a CDI Ragone plot (a) and the representative conductivity profiles (b).

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O3-2

CONTINUOUS MEMBRANE CAPACITIVE DEIONIZATION CONCEPTS BASED ON FLOW ELECTRODES – FROM A TWO TO ONE MODULE CONFIGURATION

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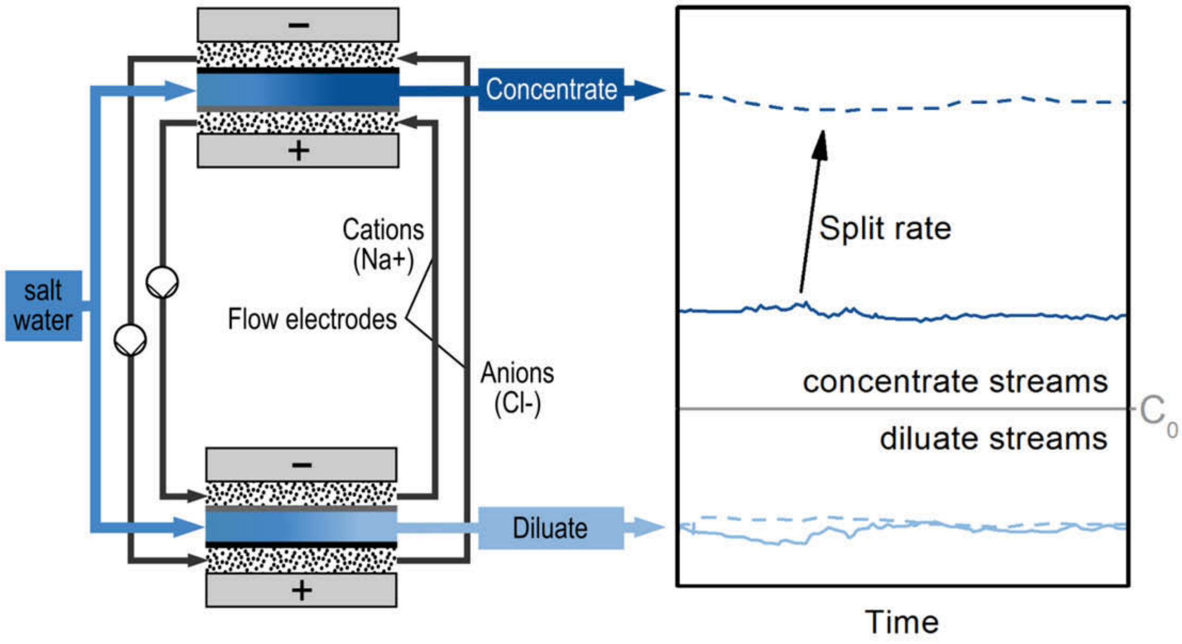
Flow-electrode Capacitive Deionization (FCDI) is an upcoming research field in Capacitive Deionization (CDI) and Membrane Capacitive Deionization (MCDI). Classical CDI and MCDI processes are limited in their performance due to the immobile electrodes with limited salt adsorption capacities. Charge-discharge cycles are needed during the operation of a CDI process, which lead to a need of complex system setups for establishing a semi-continuous process, at most. FCDI has the potential to overcome these limitations. In FCDI the immobile porous carbon electrodes are replaced by flow electrodes which usually consist of carbon suspensions, e.g. activated carbon in water. Depending on the type of FCDI architecture the flow electrodes are separated from the water stream or each other by ion exchange membranes (IEM).[1,2] Flow electrodes show high specific salt adsorption rates and additionally offer an easily scalable capacity together with the pumpability.

In this contribution we present two fully continuous processes based on FCDI which enable a simultaneous production of a diluate and a concentrate stream while the flow electrodes are continuously being regenerated. This is possible due to the recirculation of the suspensions from a charging compartment, in which water is desalinated and ions are adsorbed in the electrical double layer of the carbon particles, to a regenerating compartment with reverse charge. We were already able to demonstrate high desalination rates of up to 99 % and high water recoveries of up to 90 % with a continuous process based on FCDI in a two module configuration which is shown in the principle drawing.[3] The high water recoveries make this concept attractive, especially when comparing it to water recoveries of established desalination systems such as reverse osmosis, which usually has water recoveries of only about 50 %. A small drawback of the previously reported system is the increased energy consumption due to the application of a voltage for the desalination module as well as for the regeneration/discharge in the second module and the need of pumping energy for two flow electrodes.

To overcome these drawbacks we report a new continuous FCDI system, which only requires a single flow electrode and the application of a voltage to a single module. We were able to demonstrate desalination rates of up to 70 % and water recoveries of up to 80 % with the new system at very good current efficiencies of 0.93 and higher during continuous operation. The new system reaches lower degrees of desalination and concentration, but shows a significantly improved energy efficiency. The two suggested continuous FCDI systems could be used for applications such as desalination or the removal of ionic compounds from waste water streams.



Continuous FCDI system in two module configuration

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O3-3

FLOW-THROUGH ELECTRODE CAPACITIVE DEIONIZATION THEORY AND EXPERIMENTS

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Capacitive deionization (CDI) is a technique for removing charged species from aqueous solutions that shows great promise for applications in water desalination and wastewater treatment. At its core, a CDI cell consists of a pair of porous electrodes electronically isolated from each other by a separator layer. The feed solution flows either through or between the electrodes, which are electrically charged to drive ion migration into the electric double layers (EDLs) on the electrodes' surfaces (electrosorption). When the electrodes are discharged, the ions are released from the EDLs into the feed stream and the discharge current can be harnessed to regain energy.

The flow-through electrode (FTE) architecture, in which the feed solution passes through electrodes containing a bimodal pore structure, has seen extensive development in the past several years [1][2]. FTE has emerged as a CDI cell design that has the potential to quickly charge and adsorb ions [2], and further avenues for optimization present FTE as a promising architecture in the CDI realm. Despite the advantages of FTE CDI, a comparison between experimental results and theoretical predictions has not yet appeared in the literature. In this work, we provide a suitable theoretical model based on the Donnan description of the EDLs [3] and porous electrode transport theory. The convective-electromigration set of equations requires carefully considered inflow and outflow boundary conditions. Our experiments were performed with a custom-built FTE CDI cell consisting of two 2x2 cm activated carbon film electrodes isolated by a separator. Feed water flow rate is controlled with a peristaltic pump, and outlet flow conductivity is measured with a downstream, flow-through conductivity sensor. Experimental results are shown in Figure 1.

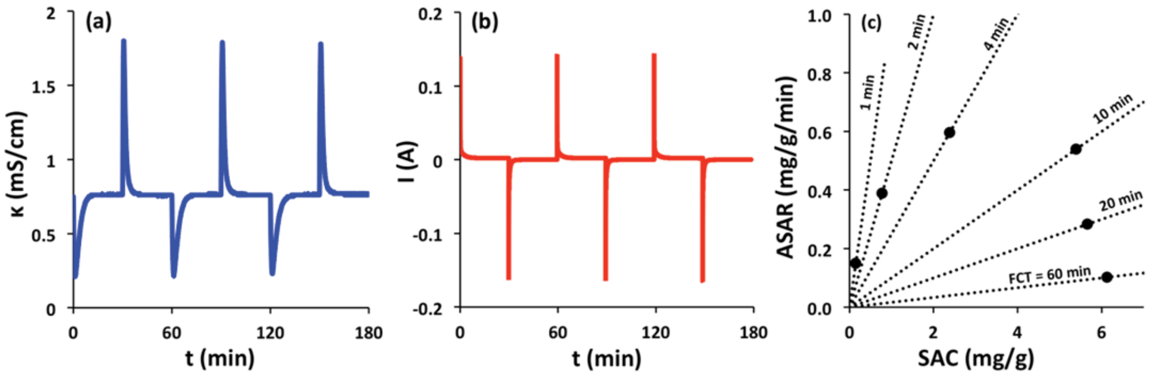

Figure 1 – Preliminary experimental results. (a) Conductivity (κ) vs. time for a 60 minute full cycle time (FCT) with three complete charge/discharge cycles shown. (b) Corresponding I-t curve for 60 min FCT. (c) Kim-Yoon plot showing average salt adsorption rate (ASAR) in mg salt adsorbed per g electrode material per minute vs. salt adsorption capacity (SAC) in mg of salt mass adsorbed per g electrode material. Dividing SAC by ASAR gives FCT, and lines of constant FCT are shown. Electrolyte solution used was 5 mM NaCl and the charging voltage was 1 V in all experiments.

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O3-4

FABRICATION AND CHARACTERIZATION OF ACTIVATED CARBON@ION-CONDUCTING POLYMER FOR WELL-DISPERSED FLOW ELECTRODES IN FCDI SYSTEM

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Our research group has suggested novel system of capacitive deionization (CDI) using flowable carbon electrode, named flow-electrode CDI (FCDI). The major benefit is that in FCDI, continuous process is possible without discharge step for electrode regeneration and scale- up is also easy [1]. It is well-known that salt adsorption rate depends on loading amount of porous carbon material. However, as the surface of porous carbon is hydrophobic, it limits high carbon material mass loading and flowability due to reaggregation. To overcome these disadvantages, we have fabricated composite electrodes with core-shell structure, composed of activated carbon (AC) coated with ion-conducting polymer, in order to improve wettability and suspension stability in aqueous electrolyte.

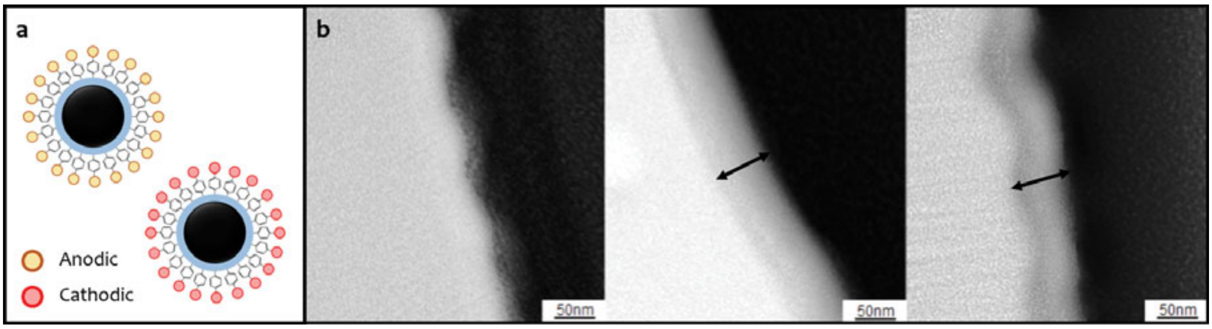

Fig 1. Schematic structure of composite electrode (a) and TEM images of polymer layers on AC surface (b)

Spherical porous AC (specific surface area, 3250 m^2/g) were used as the capacitive materials in flow electrode. For preparation of composite electrode, ion-conducting polymer layers were synthesized by radical polymerization after micelle formation by monomers on AC surfaces (Fig. 1a). Vinyl benzyl trimethyl ammonium chloride and sodium 4-styrenesulfonate were used as anion- and cation-conducting monomers, respectively. It was characterized by various analysis tools, such as transmission electron microscopy (TEM). Deionization performance was confirmed by FCDI cell according to carbon loading amount.

The thickness of coating layers is about 5 nm, irrespective of cation and anion (Fig. 1b). The AC surfaces coated with ion-conducting polymer have become hydrophilic due to functional groups, compared to bare AC. This property enables the maximum carbon loading amount to increase up to 27.5 wt%, and results in maximum desalting efficiency of 18.5% (Fig. 2). Moreover, as the functionalized carbon surface remained the same surface charge in aqueous electrolyte, it is explained that the electrostatic repulsion between carbon particles improved the suspension stability. Therefore, we expect that it is possible to apply as an excellent dispersant for decreasing its viscosity in flowable electrode with high carbon loading.

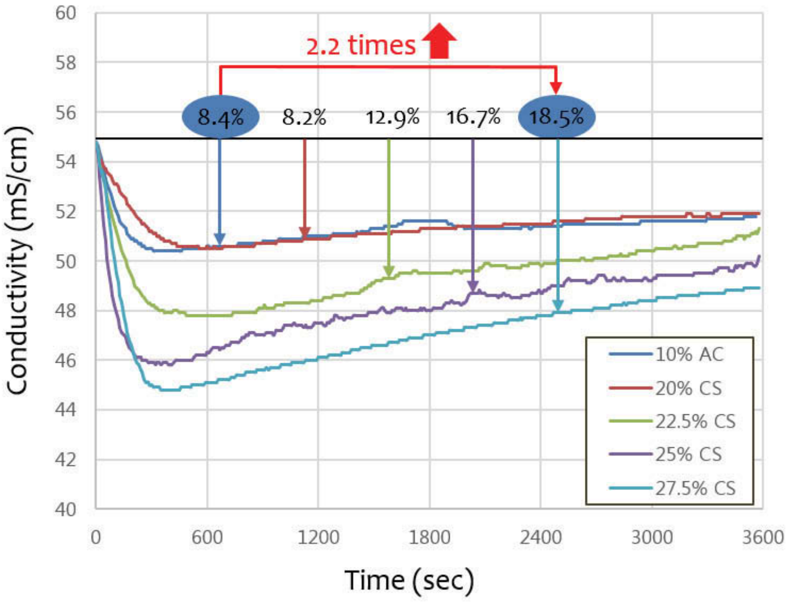

Fig. 2. Deionization performance of composite electrode using FCDI system according to carbon loading amount.

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O3-5

PLUG FLOW DESALINATION

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Introduction

Droplet microfluidics, or "digital microfluidics" [1] is an emerging approach for manipulation of extremely small volumes in the nano- and picoliter range. Droplets are generated through a junction in which two immiscible fluid phases, e.g. water and a gas, are combined. The generation speed of these highly mono-disperse droplets in size can reach hundred to kHz rates [2]. Benefits of digital microfluidics are the increase in throughput of the number of samples without scaling the total volume of sample consumption [1]. For each droplet the transport, reactions and pre-treatment steps can be controlled individually, before analysis through e.g. mass spectrometry. Desalination is a sample preparation step required for sample analysis through mass spectrometry [3] which is currently challenging to perform without breaking compartmentalization. CDI as a sample preparation method could be an attractive alternative. Swaminathan et al. demonstrated CDI of a single droplet in a static situation on two in-plane platinum black electrodes and reported 41% desalination in the bulk of 10 mM electrolyte [4]. Separation of the concentrated and desalinated solution was not demonstrated.

We demonstrate preliminary experiments on the desalination of flow plugs of an NaCl solution in a gas dispersed phase. The principle of CDI based desalination was modified into a hybrid system of non-faradaic membrane CDI on one electrode and electrochemical desalination at the second electrode. The conductivity of the flow plugs was monitored real time.

Experimental

The chip design is shown in Figure 1. The microfluidic channel is shaped in a Teflon spacer. The electrolyte concentration was measured online via a home-build conductivity cell and lock-in amplifier. First, a continuous flow experiment was performed at a flow rate of 1 μL min^{-1} , followed by a plug flow desalination experiment. Plugs are generated in a y-junction coupled to the chip via tubing. The flow rate of the water was 2 μL min^{-1} and of the nitrogen gas ≈1 SCCM.

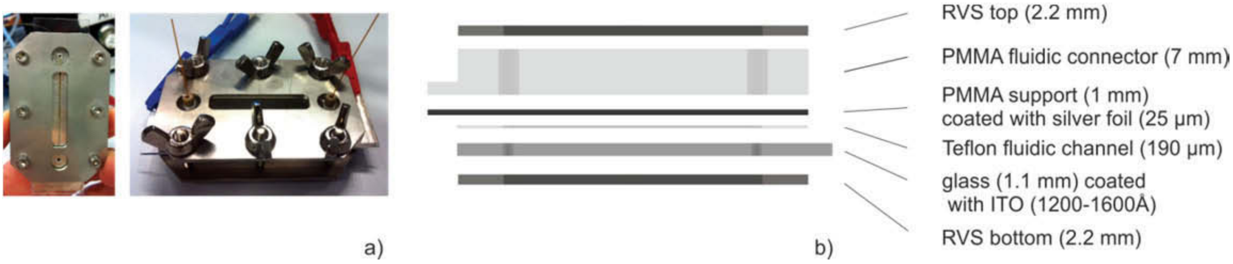

Figure 1 a) Picture of the bottom (left) and top (right) of the chip. b)Schematic side view. The RVS top and bottom together form a clamp. The upper electrode is fabricated from silver. Upon the application of a sufficiently large oxidizing potential, silver and Cl$^-$ ions react to form AgCl at the electrode. The bottom electrode consists of an indium tin oxide electrode coated with a cation exchange membrane, which stores the electrostatic removed Na$^+$ ions from the solution. The top and bottom electrode are connected via a crocodile clamp on each side of the chip.

Results and discussion

The potential and determined concentration as a function of time for continuous flow experiments are described in Figure 2 a) and b), respectively. From the continuous flow experiment a desalination percentage of 62.5% was observed. For the plug flow desalination a minimal desalination percentage of ≈ 3.5% is observed. Improvement of this percentage can be achieved by decreasing the flowrate and increase the surface-to-volume ratio of the electrodes in the microfluidic channel as well lengthen the residence time of the flow plugs in the chip.

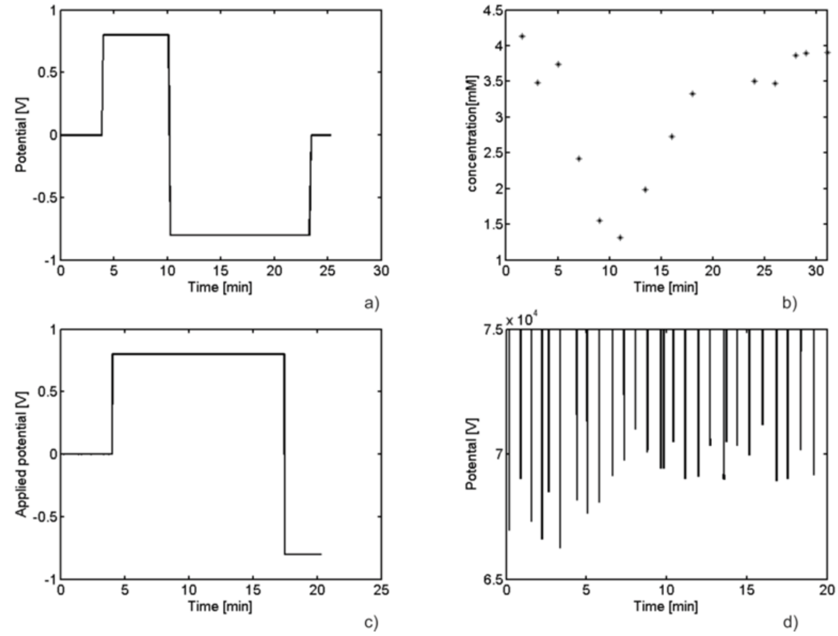

Figure 2 a), b) applied desalination potential and measured concentration at the outlet of the desalination chip as a function of time for continuous flow measurements c), d) potential and lock-in measurements of plug flow desalination.

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SESSION 4: FARADAIC CDI

O4-1 (invited)

THEORETICAL MODELING OF MIXED CAPACITIVE-FARADAIC PROCESSES IN CDI

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Capacitive Deionization (CDI) removes salt from water by making use of the Electrical Double Layer (EDL) phenomenon where electronic charge in the carbon matrix of capacitive electrodes is exactly charge-compensated by ionic charge in the electrolyte phase within micropores [1]. When a net adsorption of ions results, the two-electrode CDI cell absorbs salt from the water.

Theories of the EDL structure describe the amount of stored charge versus cell voltage, as well as the ionic components of charge, and thus predict the ratio of counterion adsorption into the electrode, over coion depletion from the electrode. For CDI, various EDL models have been proposed: Newman introduced the Helmholtz model [2], while Kastening developed the concept of the Donnan model [3]. Later work made use of the Gouy-Chapman-Stern (GCS) model for CDI [4]. In this presentation, these three modeling approaches are briefly compared.

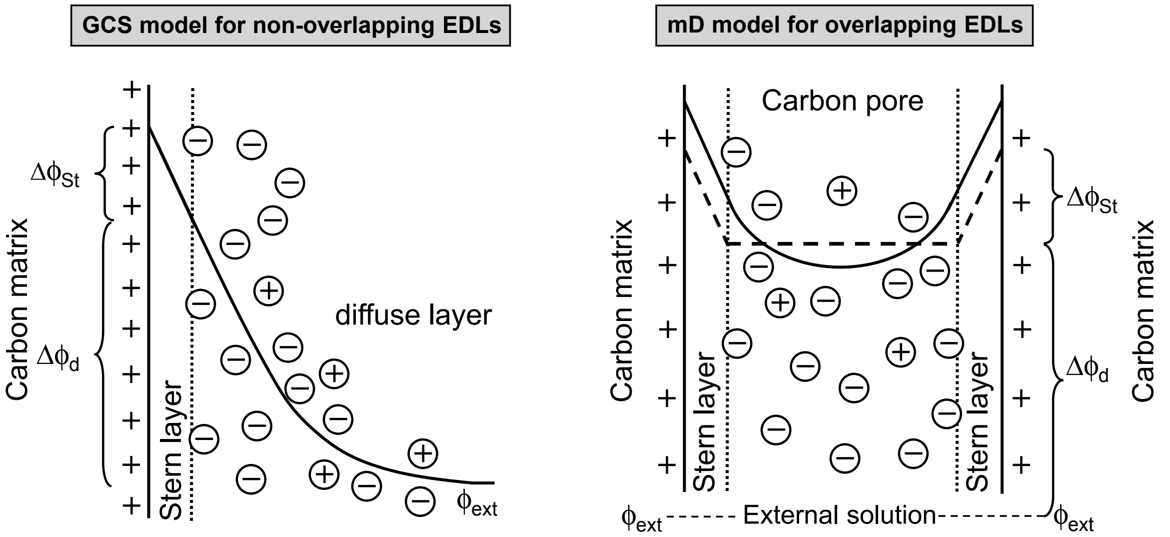

Figure 1. Qualitative comparison of two EDL models, the GCS-model (left) and the Donnan model (right) to describe the micropore EDL structure in carbon CDI electrodes.

Most modern developments in CDI modeling make use of the Donnan model which is mathematically easy to use and can be robustly implemented in porous electrode transport theory [5]. The Donnan model very accurately predicts both salt adsorption and charge in a two-electrode CDI cell [6]. Results of fits to data using the Donnan model are presented.

In the second part of this presentation, the Donnan model is extended to include an extra source of charge, namely fixed chemical charge, residing in the carbon micropores [7]. It was recently discovered how this modified Donnan model can explain the puzzle of inverted operation of CDI. At the same time, this EDL model predicts the existence of a range of CDI operation with significantly increased salt adsorption.

All of the above models only describe the capacitive behavior of CDI electrodes. However, in CDI electrodes also Faradaic/redox reactions can occur, such as the oxidation of the carbon, or the storage of protons and electronic charge in the reaction quinone + H^+ + e^- ↔ hydroquinone. For a full understanding of electrode behavior in CDI, also such reactions must be included.

Here a modeling framework is presented that extends EDL theory to include Faradaic reactions at the carbon surface, following the approach presented by Frumkin in 1933 [8]. In this way, we develop a model combining capacitive and Faradaic processes in CDI, considered one of the most challenging topics in electrochemistry. We present calculation results of the behavior of CDI electrodes with Faradaic reactions for chronoamperometry (switching between fixed voltage levels) and for cyclic voltammetry.

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O4-2

PSEUDOCAPACITIVE DEIONIZATION: REDOX-MEDIATED ELECTROSORPTION OF ANIONS

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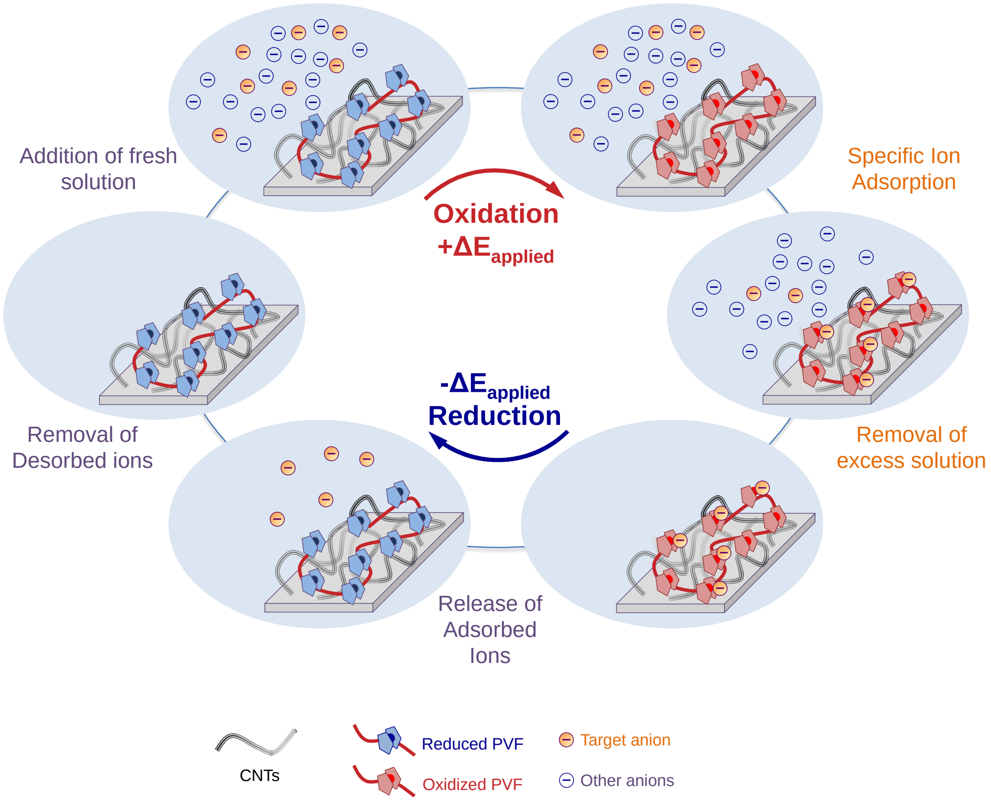
Capacitive deionization systems are very attractive due to the flexibility of control through modulation of electrochemical potential, fast kinetics and possibility of energy recovery and integration with renewable sources.[1] However, conventional capacitive deionization relies on the excess ion accumulation in the double layer, and can in only very few cases remove one ionic species over another. In particular, selective electrosorption and release of target anions is of fundamental as well as practical interest for separations in chemical processes and environmental waste control.[2] Our approach relies on heterogeneous redox-active species to mediate the specific interactions with target anions, as well as take advantage of the large pseudocapacitive charge to provide faster kinetics, higher ion adsorption capacity and energy recovery performance.

We report the use of heterogeneously supported redox-organometallics, namely metallocenes, for the sorption and release of specific anions from and to the liquid-phase under oxidizing and reducing conditions, respectively, in both organic and aqueous media.[3] Rather than rely solely on adsorbate charge or size, these redox-functionalized electrodes, through their electrochemical response to an applied potential, regulate the specific chemical interactions of the supported-organometallics with target functional groups of anions to achieve reversible and stoichiometric binding. We explore the mechanisms of this selective interaction through various spectroscopic methods, electrochemical characterization and electronic structure calculations.

Overall, electrochemically redox-mediated interactions are a novel approach for achieving anion specificity that goes beyond solely capacitance. Furthermore, the redox-active species provide large pseudocapacitance that significantly enhances the kinetics and energetics of the system over standard double-layer effects. We aim to further broaden our library of adsorbents by integrating the materials development of conductive supports with the chemical design of various redox centers. This technology is of scientific and economic interest for (1) sustainable water remediation and waste control, through the removal of highly toxic aqueous contaminants such as organic anions present in agricultural or industrial waste, and (2) improving chemical processes, as a powerful method for direct purification of charged products in chemical synthesis.



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O4-3

POTENTIAL OF ZERO CHARGE MODIFIED CARBON ELECTRODES FOR CDI AND MCDI APPLICATIONS

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Capacitive deionization (CDI) is an emerging salt removal technique based on the formation of electric double layers in porous electrodes. Unlike alternative de-salting technologies like reverse osmosis or distillation that functionally separate water from salt content with the respective aid of added pressure or heat, CDI electrostatically targets the salt content instead, making it particularly attractive for the treatment of mid (brackish water) to low (drinking water) concentration salt streams, where alternative technologies do not possess comparative energy consumption benefits. In addition, CDI offers the possibility of energy recovery in the convenient form of electricity, which can be used to directly power subsequent CDI units, or other auxiliary devices. CDI can be further improved via the incorporation of membranes to form what is popularly regarded as membrane-assisted capacitive deionization (MCDI). In MCDI, complementary ion-exchange membranes (IEMs) are placed next to porous carbon electrode pairs to increase desalination performance by mitigating losses that result from converting electronic to ionic charge at the electrode-electrolyte double layer. While the addition of membranes increases the cost for constructing the deionization system, the resulting benefit to deionization performance and efficiency warrants its continued research and use.

The CDI/MCDI field has received much attention in recent years, and new materials, models, and operation modes have been developed to provide increased salt capacity, deionization rates, efficiency, system predictability and control, and device performance longevity. The potential of zero charge (PZC), i.e., potential at which there is no net charge on the electrode, has been demonstrated to be pivotal to realizable desalination performance, dynamic response, efficiency, and longevity in both CDI and MCDI systems(1-4). In the work presented here, the dynamic response and performance of symmetric and asymmetric PZC electrode combinations in CDI and MCDI cell setups will be shown. In addition, the impact of PZC location on long-term performance will be presented. Finally, new operation modes, including a completely inverted capacitive deionization process, will be shown that makes use of chemical surface charge in the removal of ionic content. Future work to enhance the separation capacity and efficiency of these systems will be mentioned.

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O4-4

HYBRID CAPACITIVE DEIONIZATION SYSTEM WITH SODIUM IRON PYROPHOSPHATE

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Capacitive deionization (CDI) has attracted great attention in terms of novel convergence with energy and water technology. CDI is an energy efficient and eco-friendly desalination technology in which ions are stored and released in an electrical double layer with porous carbon materials. Recently, Hybrid-CDI (HCDI), which combined system with porous carbon and sodium intercalated metal oxide material was proposed. HCDI showed superior ion removal rate and capacity. This system provides an opportunity to overcome the limitation of CDI system of which insufficient deionization performance.

In this study, it was investigated that HCDI system consists of sodium iron pyrophosphate ($Na_2FeP_2O_7$), anion exchange membrane and activated carbon (MSP20). In this system, sodium ions are intercalated in the sodium iron pyrophosphate electrode, and chloride ions are captured on the surface of the activated carbon electrode. The crystal structure of sodium iron pyrophosphate exhibited the triclinic space group, P1, which is described by vectors of unequal length, as in the orthorhombic system. In this sodium iron pyrophosphate electrode, sodium ions are intercalated/de-intercalated with electrochemical activation based on Fe^{2+}/Fe^{3+} redox couple reaction. The deionization capacity was measured as about 29 mg g-1 (milligrams of sodium chloride ions per grams of activated materials of both electrode) at 10 mM of NaCl electrolyte. Thus, HCDI is a promising system for desalination with superior performance in capacitive techniques.

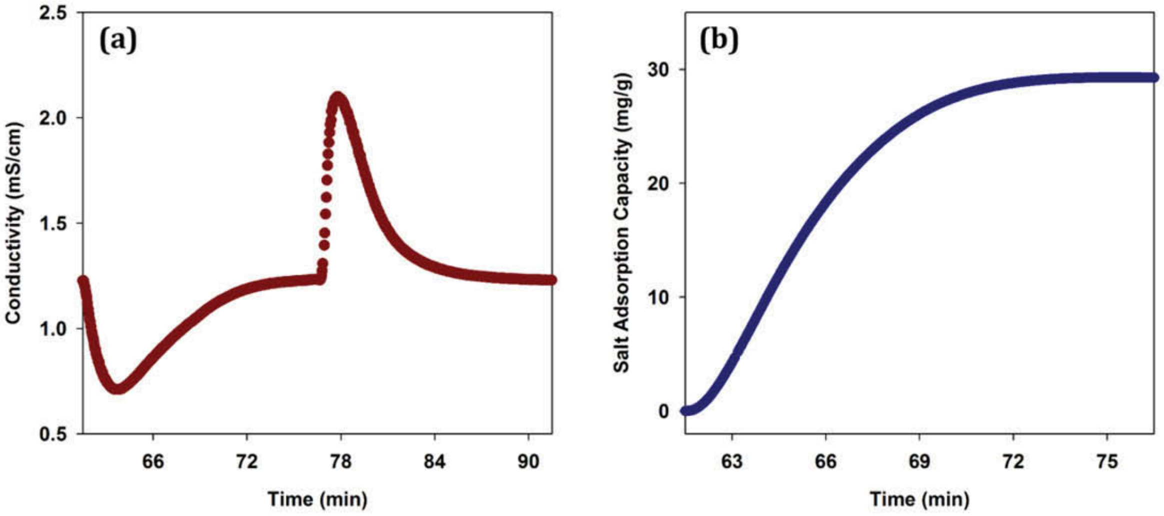

Figure 1 Representative desalination performance of the HCDI system. (a) The conductivity changes of the effluent at 3rd cycles. The operation was carried out in 10 mM of NaCl (1.2 V for 15 min and -1.2 V for 15 min). (b) Ion removal capacity and accumulated ion removal rate of HCDI during the 3rd ion capturing step, represented as the mass of deionized ionic charge (mg) per mass of the sodium iron pyrophosphate and activated carbon electrodes (g).

O4-5

HYBRID ELECTROCHEMICAL INTERFACES FOR CONTROL OVER SEPARATION AND CATALYTIC PROCESSES

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The ability to exert control over an entity or a process is arguably the ultimate demonstration of our understanding of that process, and enables the full exploitation of its potential. Our research aims to establish design principles for efficient electrochemical interfaces, and develop novel electrochemical modulation strategies for separation and catalysis applications. An electrochemical interface generally consists of three key components: the electrode phase, the electrolyte phase, and the functional layer between these two phases. Rational design of an electrochemical interface for a specific application requires careful consideration of these three key constituents and the simultaneous electron/ion transport process across the interface. Identification of the critical factors that govern the efficiencies of electrochemical interfaces is also important for other future technologies of relevance to energy, the environment and health care.

In this paper, we will discuss electrochemistry-based control strategies for several separation and catalytic processes, using electrochemically responsive polymer/carbon hybrid systems with optimized structural, electronic, and chemical properties. First, we will show a new electrochemical mediation strategy for separation of organics-water mixtures using materials that exhibit redox-tunable hydrophobicity, and for separation of ion-ion mixtures using materials that bear stimuli-controlled charge densities. Second, we will introduce a catalysis control concept, electrochemically responsive heterogeneous catalysis (ERHC), that allows for temporal and spatial control of reaction kinetics and product selectivity in both batch and flow systems. In these examples, special attention is paid to (i) interrogating the relationship between electrochemical activities of material systems and the overall efficacies of separation or catalytic processes, (ii) comparing electrochemical modulation approaches to conventional methods in terms of energy consumption, and (iii) identifying general descriptors for high selectivity in separation and catalysis based on molecular-level interactions between target species and redox moieties.

SESSION 5: SPECIAL ION REMOVAL

O5-1 (invited)

ELECTROSORPTION TECHNOLOGY FOR HEAVY METAL REMOVAL FROM WASTE WATER

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Heavy metal pollution has been a serious problem in China. The major contamination sources are electroplating and mining industries. As electrosorption technology (also called capacitive deionization) is an effective means to remove various ions from water phase, study has been carried out to investigate the effectiveness of such technology in reduce the heavy metal discharge in electroplating waste water. Filed pilot tests have been conducted for different electroplating waste streams, and results showed that electrosorption technology is well suitable for remove heavy metals such as copper, nickel, chromium and others. The waste streams after treatment all reached the criteria of CEPA discharge codes. The tests also showed that the heavy metal removal with electrosorption technology is more efficient when waste steam pH is in the range of pH 1.3 to 2.5, which is typical in real industry situations. Therefore, it is possible to treat the electroplating waste stream directly without neutralization process upfront as traditional treatment process. The cost of treatment could be lowered thereafter.

O5-2

BATCH AND SINGLE PASS STUDIES OF FLUORIDE AND NITRATE REMOVAL FROM BRACKISH GROUNDWATERS BY CAPACITIVE DEIONIZATION

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In this work, the feasibility of fluoride and nitrate removal from brackish groundwaters by single pass and batch-mode CDI was investigated. These anions are present in subsurface waters at troublesome levels in regions of South Asia, Africa and the Middle East. The prescribed levels for these two contaminants such as to be deemed potable is of the order of 1 and 50mg/L for fluoride and nitrate respectively. There are a range technology that can treat water containing naturally found levels of fluoride and nitrate to these prescribed levels such as adsorption, ion exchange, reverse osmosis and electrodialysis, each with their own limitations. CDI can potentially fill the gap left by these other technologies with a clear need now for application development in this space that addresses performance characterization and identifying limitations subject to typical constraints found on location at sites with contaminated groundwater. This work brings together these elements with electrode modeling used to focus on ion selectivity of trace contaminants in the context of subsurface waters containing up to 3000mg/L salt concentration. We identify ion selectivity as the key to understanding the performance, but more importantly, the limitations of CDI in guaranteeing supply of potable quality water in rural/remote applications. We also look at the sensitivity of ion selectivity to engineering parameters such as flow rate, voltage and electrode area.

In our experimental study, the effects of flow rate, initial fluoride concentration, and initial coexisting NaCl concentration on fluoride removal were studied for batch and single-pass systems. A simplified one-dimensional transport model for dual anions was developed and found to reliably describe the dynamic process of removal of both fluoride and chloride ions in CDI cells over a range of well-defined operating conditions (Figure 1).

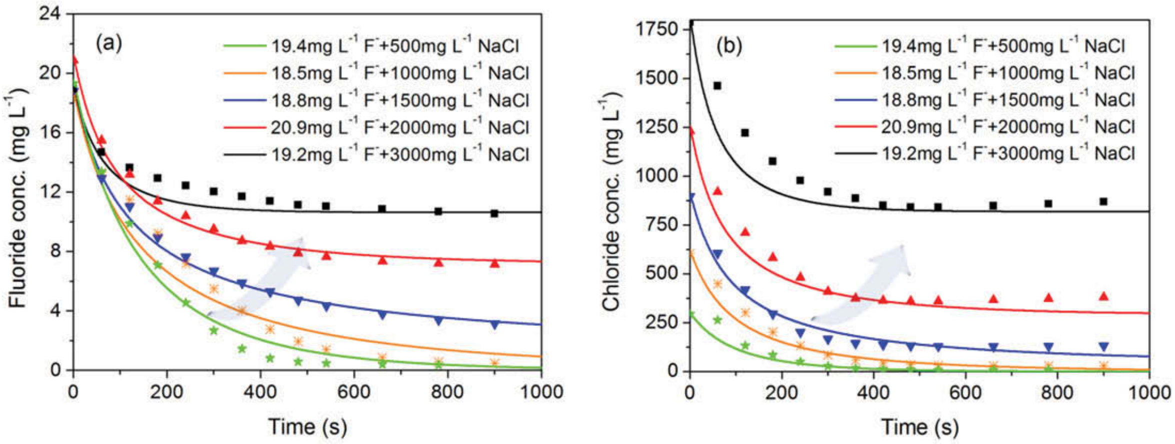

Figure 1. Effects of initial coexisting NaCl concentration on (a) fluoride and (b) chloride batch-mode removal processes. Experimental conditions: V_{tot}=11.7 L, V_{cell}=1.6 V, u=4.6 L min^{-1}. Symbols: experimental data; Lines: modeling results.

Based on the ability of the model to describe fluoride removal, it was extended to description of nitrate removal from brackish groundwaters and also found to perform well (Figure 2). Thus, the approach to description of ion removal, at least in batch studies, appears robust and should assist in optimization of design and operating conditions such that optimal removal of trace ionic species is achieved even when high background concentrations of salt are present. In our single pass experiments we observe similar capability which allows for flexibility in process configuration.

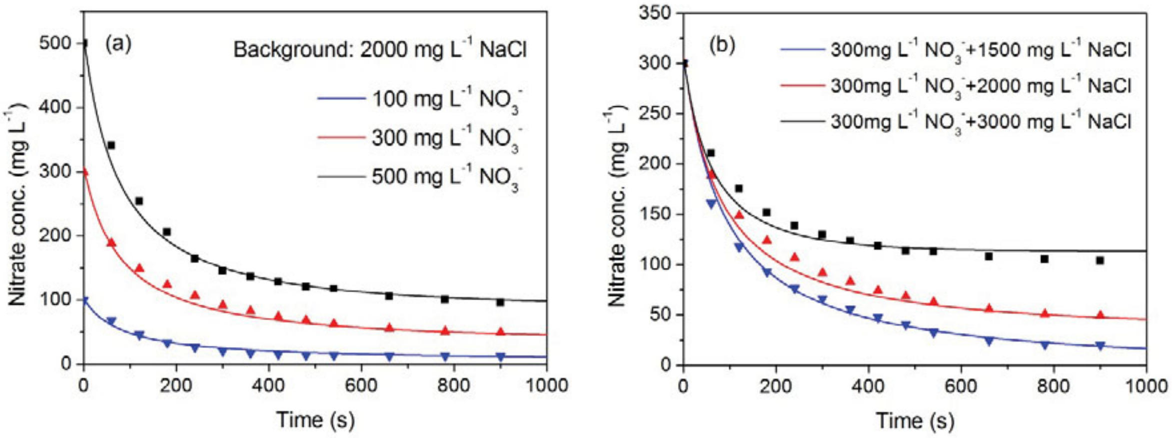

Figure 2. Electrosorption kinetics for batch process of nitrate (a) at different initial nitrate concentration (100 mg L^{-1}, 300 mg L^{-1}, 500 mg L^{-1}) in the presence of initial 2000 mg L^{-1} NaCl, and (b) at different initial NaCl concentration (1500 mg L^{-1}, 2000 mg L^{-1}, 3000 mg L^{-1}) in the presence of constant initial nitrate concentration (300 mg L^{-1}). Experimental conditions: V_{tot}=11.7 L, V_{cell}=1.6 V, u=4.6 L min^{-1}. Symbols: experimental data; Lines: modeling results.

O5-3

INVESTIGATION OF REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS BY CAPACITIVE DEIONIZATION

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Capacitive deionization (CDI) is a novel water purification technology for the removal of ions with the features of low-energy consumption, no membrane component, no secondary waste, and easy regeneration of electrodes [Anderson et al., 2010]. The working principle of the CDI system is to apply an external electric field on a pair of porous carbon electrodes, and thereby ions can be electrostatically captured onto the oppositely charged electrode surface. Notably, our previous study reported that copper ions can be effectively removed from solutions by electrosorption and electrodeposition [Huang et al., 2014]. The removal mechanism has a dependency on the amplitude of applying electric voltage. However, researches related to heavy metals removal with CDI technology are still limited.

The main object of this study is to provide a fundamental aspect of heavy metal removal in CDI process using activated carbon electrodes. Divalent heavy metals with different reduction potentials [Bard et al., 1985] are selected, such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Ca^{2+}, for the following experiments: electrochemical characterization and CDI tests. Cyclic voltammetry and electrochemical impedance spectra measurements are carried out to clarify the relationship between heavy metals and activated carbon electrodes. A batch-mode CDI cell was performed at an applied voltage of 1.2 V to remove divalent heavy metal ions at 1 mM. After the CDI process, the electrode surfaces are further analyzed by SEM, EDX, and XPS for determining the removal characteristics of divalent heavy metals onto the carbon electrodes. According to the results, the divalent heavy metals can be successfully removed by CDI process. The removal mechanism is not only by electrosorption of electrical double-layer charging, but also by the electrodeposition of reduction of metals onto the electrode surface. More specifically, the reduction potential of divalent heavy metals plays an important role to determine their electrochemical behaviours during the CDI process. For example, Zn^{2+} ions with a lower reduction potential (Zn^{2+} /Zn, $E^0=-0.76$ V) are mainly removed by electrosorption, which is further confirmed by depolarizing the electrode. In contrast, Cu^{2+} ions, possessing a high reduction potential (Cu^{2+} /Cu, $E^0= +0.34$ V), have a tendency to be reduced to be cuprous oxide in CDI. The electrodeposition of Cu^{2+} ions on the electrode surface are also observed by SEM, EDX, and XPS. Furthermore, the removal selectivity is studied by a mixture of Zn^{2+} and Cu^{2+} ions to investigate the competition between different divalent ions. As evidenced, Cu^{2+} ions are preferred to be separated from water than Zn^{2+} ions. The research findings can provide useful information to understand the removal characteristics of different heavy metals with CDI technology for water purification and wastewater treatment.

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SESSION 6: ENERGY HARVESTING

O6-1 (invited)

APPLICATION OF THE ELECTROSORPTION PROCESS FOR ENERGY GENERATION

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Where solutions of different composition come together, energy is available. For instance, in the situation of a river discharging into the sea, power equivalent to a two hundred meter drop of the river can be generated. This so-called “Blue Energy” is a substantial clean renewable energy source. The challenge is to develop technology that is able to harvest this source in a clean, efficient and cost-effective way.

When two different solutions are directly mixed, the energy is directly dissipated as mixing entropy and no energy can be harvested. The basis of any technology is therefore selective mixing, where either the salt is transferred from the concentrated to the dilute solution, or water is transferred from the dilute to the concentrated solution.

There are several technologies available for generating energy from mixing two solutions. Pressure Retared Osmosis and Reverse Electrodialys are most advanced in development and both have been tested at pilot scale. Electrosorption using porous electrodes is an attractive alternative process for this type of energy generation. The porous electrodes can be made selective for ion adsorption via applying either an electrostatic potential, a fixed surface charge, or a membrane. Electricity is directly produced and a secondary converter like a turbine or electrode reaction is not needed. The state of the art will be discussed together with challenges ahead and new applications like generating energy from CO_2-emissions.

O6-2

NEW LOW-COST HEAT-TO-CURRENT CONVERTERS CAN BE BUILT FROM CONVENTIONAL SUPERCAPACITORS

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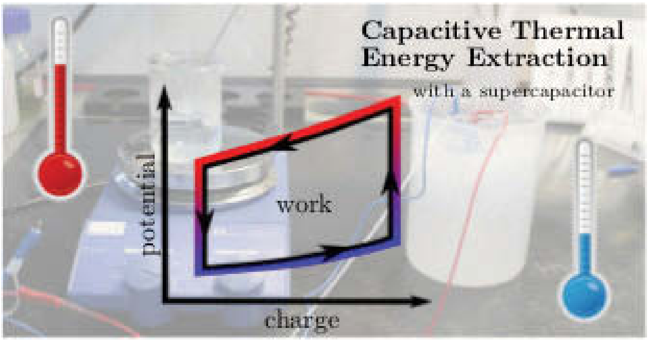
Thermal energy is abundantly available, and especially low-grade heat is often wasted in industrial processes as a by-product. Tapping into this vast energy reservoir with cost-attractive technologies may become a key element for the transition to an energy-sustainable economy and society. We propose a novel heat-to-current converter which is based on the temperature dependence of the cell voltage of charged supercapacitors. Using a commercially available supercapacitor, we observed a thermal cell-voltage rise of around 0.6 mV/K over a temperature window of 0 °C to 65 °C. Within our theoretical model, this can be used to operate a Stirling-like charge-voltage cycle whose efficiency is competitive to the most-efficient thermoelectric engines. Our proposed heat-to-current converter is built from cheap materials, contains no moving parts, and could operate with a plethora of electrolytes which can be chosen for optimal performance at specific working temperatures. Therefore, this heat-to-current converter is interesting for small-scale, domestic, and industrial applications.



O6-3

CALORIMETRY OF ELECTRIC DOUBLE LAYER FORMATION AT CDI ELECTRODES

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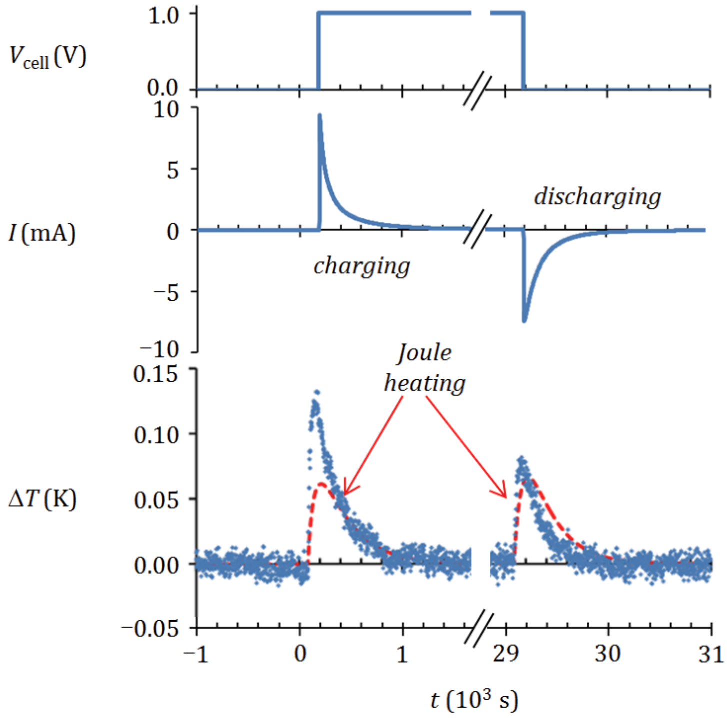
The entropy of ions in the pores of an aqueous carbon electrode decreases upon charging and increases upon discharging. In theory, these changes are accompanied by heat release to the water upon charging and heat removal from the water upon discharging. Moreover, it has been argued that the ensuing temperature effects are beneficial to the thermodynamic cycle efficiency of blue energy technologies such as capmix and desalination by capacitive deionization [1]. The challenge to test these predictions experimentally fits well with our background in electrochemistry [2-4] and colloid science, including the study of electric double layers [5,6]. Here, we will present calorimetric confirmation of heat exchange due to changes in ion entropy inside aqueous porous carbon electrodes that were kindly provided by Biesheuvel [7,8].

A typical result is shown in Figure 1. A cell voltage is applied between two porous carbon electrodes in aqueous salt solution (V_{cell}), the current is measured (I), and from these data and from the time constant, heat capacity, and electric capacitance of the electrochemical cell, the time-dependent temperature change (ΔT) due to Joule heating is estimated. The total heat measured by differential calorimetry is higher than the Joule heating when the electrodes are being charged, and it is lower when the electrodes are being discharged. In contrast to Joule heating, which is always exothermic, the ion entropic heat effect is thus found to be exothermic for charging and endothermic for discharging, as expected from theory. Moreover, within experimental error, the absolute value of the heat from ion entropy change is the same for charging and discharging, about 20% of the total heat measured. Systematic measurements are currently being performed as a function of cell voltage and ionic strength, for quantitative comparison with theory. The thermal effects are small but measurable, and they offer new independent insight into the thermodynamics of electric double layer formation in porous electrodes for CDI and capmix.

Figure 1.



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O6-4

EFFECT OF ELECTRODE MATERIAL SELECTION ON THE ENERGY PRODUCTION BY DOUBLE LAYER EXPANSION

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The capacitive mixing procedure for energy extraction based on Double Layer Expansion (CDLE) belongs to the group of so-called CAPMIX techniques [1-3], which aim at obtaining energy from the salinity difference between fresh and sea waters. Specifically, the CDLE technique takes advantage of the voltage rise that occurs when sea water is exchanged for river water in a pair of porous electrodes which jointly behave as an electrical double layer supercapacitor. In this communication, we deal with some experimental aspects that are key for optimizing the extracted energy, and have not been analyzed yet with sufficient detail. This investigation will help in evaluating some material parameters which need to be fixed in a future CDLE device. These include the porosity and hydrophilicity of the carbon [2] and the salinity differences between salty and fresh waters.

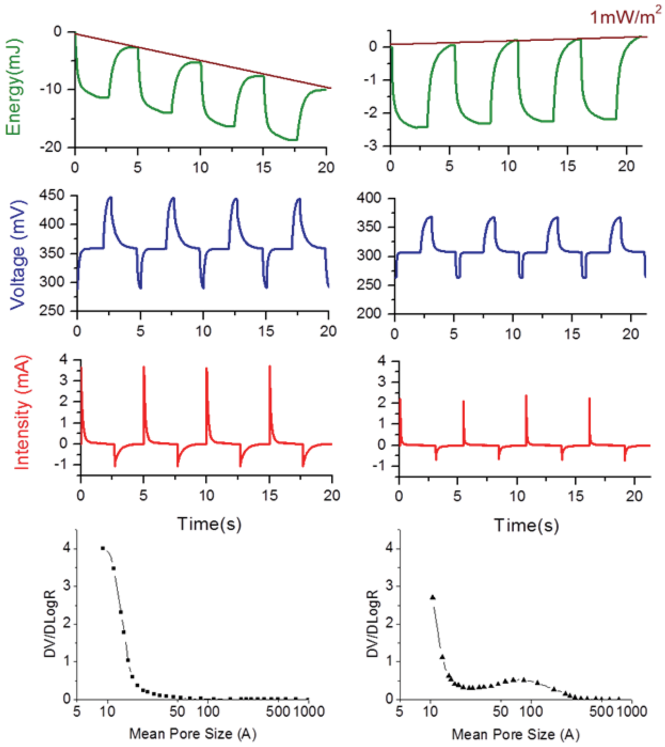

Figure 1. Voltage, intensity and energy in successive CDLE cycles for carbon electrodes with the indicated pore size distributions.

Since this technique depends on an external electric energy source, leakage is a crucial problem, since it can result in energy losses in excess of the produced energy. In this sense, it has been shown that, while the capacitance is large, the available surface for the salinity exchange is only the 10% of the total surface area [4], suggesting that having a large volume fraction of micropores may be a drawback. In this contribution we examine the role of the pore size on the relevant quantities of the CDLE cycle, that is, the delivered and extracted charge and the voltage rise upon salinity exchange (Fig.1). It is found that energy production based on electric double layer expansion can be significantly improved if electrode materials are properly selected. The average pore size, in relation with the EDL thickness and the ion diameter is, as expected, a determinant quantity. Optimum CDLE results will be obtained if the carbon used in the electrodes has a predominant pore population in the 1 nm region. We show that, although carbon electrodes with smaller pores provide larger surface area, they are not able of producing net energy. The presence of carbon particles with such pore size allows us to obtain a moderate power of up to 6.1 mW/m2, for optimum selection of charging voltage, cycle duration and load resistance.

Acknowledgements

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O6-5

A NOVEL VARIABLE CAPACITANCE ENGINE USING PERIODICALLY SQUEEZED LIQUID BRIDGES

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Variable capacitance engines operate by charging and discharging electrodes at alternating high and low capacitance, respectively. The energy harvested by an engine during a cycle is transferred from its surroundings into the system through the change in capacitance.

A lot of work in recent years has focused on electrolyte-filled nanoporous supercapacitors where variable capacitance of the electric double layer is achieved by changing the properties of the *electrolyte.* Examples include variations in concentration in capacitive mixing [1], variations in temperature in capacitive thermal energy extraction [2], or even combinations thereof [3].

In this talk I discuss a capacitive engine whose variable capacitance is caused by a change in *geometry*, brought about by a mechanical stimulus [4,5]. This system could for instance be used to harvest mechanical energy from ambient vibrations. As such this system could provide a valuable alternative to batteries in portable electronic devices which require only small amounts of electric power.

The engine consists of two parallel capacitor plates bridged by liquid droplets, a bias voltage source, and a resistive load R. An oscillation in plate separation $L(t)$ leads to a variable droplet-electrode contact area $A(t)$ hence variable capacitance $C(t)$.

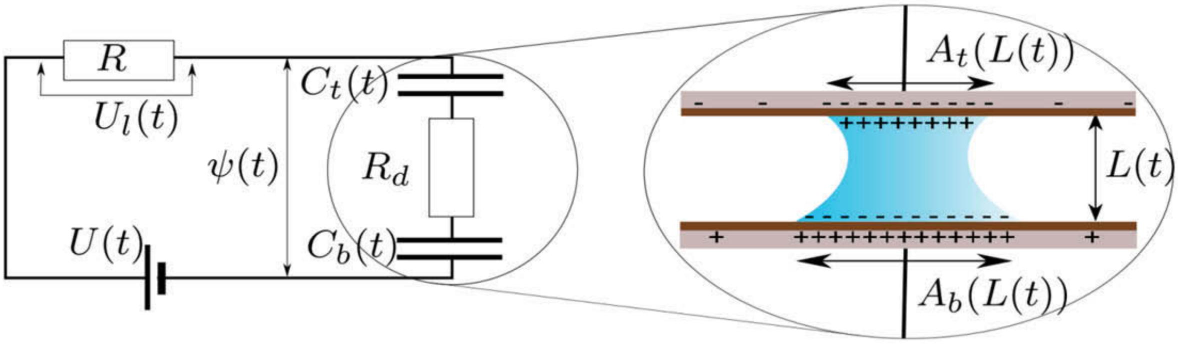

Fig 1. Equivalent circuit model of the model engine (left). Instantaneous droplet profile (right)

We present a simple equivalent circuit model, where the capacitance of the droplet-electrode interface is determined by solving the Young-Laplace equation for the droplet shape. This analysis goes beyond the present (experimental) studies which use an empirical description for the plate capacitance. Especially when the plate separation is of the order of the capillary length (typically ~3mm), effects of gravity gain importance and should not be neglected. We identify optimal operating regimes for all system parameters and, making the connection to thermodynamics explicit, show a close resemblance to CAPMIX.

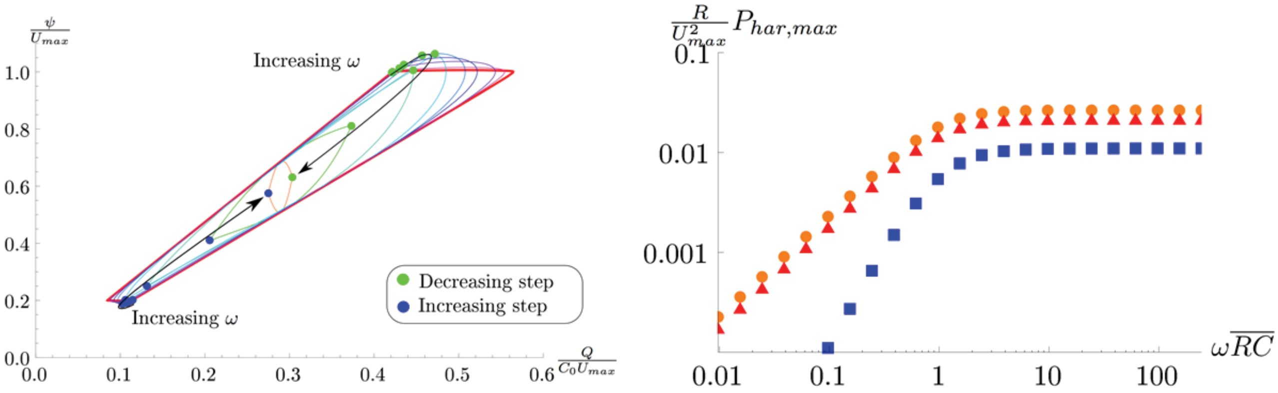

Fig 2. Charging-discharging cycles for a sinusoidal plate separation and square wave driving bias potential for a set of oscillation frequencies (left). The dependence of the harvested power on the oscillation frequency for a constant (blue squares), sinusoidal (red triangles), and square wave (orange circles) driving potential.

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SESSION 7: ION PROCESSES

O7-1 (invited)

SELECTIVE REMOVAL OF SPECIFIC ION IN CAPACITIVE DEIONIZATION

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With the increasing importance of desalination technologies, research on capacitive deionization (CDI) has been performed all over the world. CDI is a desalination technology that removes ions by electrostatic attraction on the charged carbon electrode. It is known to be a more energy-efficient and environmentally friendly process than competing technologies such as reverse osmosis (RO) and electrodialysis (ED). In addition, CDI has a much greater water recovery rate than RO, generally up to 90%. Because of the aforementioned advantages, CDI is evaluated as a promising future desalination technology.

The carbon electrode is the core element that determines the performance of CDI. Many carbon electrodes with high desalination performance have been developed using various carbon materials, such as activated carbon, carbon fiber, carbon nanotubes, aerogel, and graphene. Moreover, some researchers have improved the adsorption performance of their carbon electrodes by modifying the pore size and the surface functional groups of the carbon materials. In addition, a carbon electrode coated with an ion-exchange polymer was developed to improve the charge efficiency during the adsorption and desorption process.

Generally, the feed solution contains various ions that are in actual desalination sites. When the electric potential is applied to the electrode, all positive ions are adsorbed onto the cathode, and all negative ions onto the anode. Occasionally, however, it is desirable to remove specific ions rather than all ions from the feed solution. For instance, only calcium or magnesium ions need to be removed from a feed solution for water softening purposes. Removal of additional ions uses unnecessary energy. The selective removal of a certain ion has the advantages of low-energy costs and high-throughput in the CDI operation. This work evaluates the feasibility of the selective removal of a specific ion with CDI.

During CDI, ions are adsorbed at the surface of a charged carbon electrode. The number of ions adsorbed may depend on the features of the ions, such as concentration, valences, and mobility. However, if there is a conducting layer between the carbon electrode and the feed stream, ion adsorption can be affected by the layer. In this case, it is expected that the number of adsorbed ions is proportional to the concentration in the layer phase not the feed stream.

Based on this simple hypothesis, the possibility of the selective removal of a specific ion from a mixed solution using the membrane capacitive deionization (MCDI) cell was examined, where ion-exchange membranes are attached to the front of the carbon electrodes. It was expected that selective removal could be accomplished if the ion-exchange membrane used in the MCDI cell was highly selective toward a specific ion in the feed solution. In general, cation-exchange membranes show high selectivity to divalent cations rather than monovalent cations. Desalination experiments were conducted with the MCDI cell for a mixed solution of sodium, calcium, and magnesium ions. The adsorption results show that the ratio of adsorbed ions is proportional to the selectivity of each ion in the cation-exchange membrane used in the MCDI cell.

Additionally, a carbon electrode coated with an anion-exchange resin powder with high selectivity toward the nitrate ion was fabricated. Desalination experiments were performed for the feed solution containing chloride, nitrate, and sulfate ions. The results showed that the number of nitrate ions adsorbed at the prepared electrode was approximately two times higher than that of the conventional carbon electrode. In addition, the ratios of the adsorbed ions were strongly related to the selectivity of each ion in the resin coated on the carbon electrode.

It was known that the current density applied to the cell affected the selective removal of specific ions during the CDI process. When the current density increased, the degree of selective removal decreased. When the feed solution was supplied without current being applied to the cell, the adsorption equilibrium between the resin and the ions in the solution was maintained. The fraction of ions in the resin, however, deviated from equilibrium as current was supplied, resulting in a decrease in selective removal as the current density was increased. From this study, it can be concluded that high selectivity toward a specific ion and a rapid adsorption equilibrium are the important factors necessary to increase selective removal during CDI.

Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2014R1A1A2056082).

O7-2

EFFECTS OF SURFACE TRANSPORT ON WATER DESALINATION BY CAPACITIVE DEIONIZATION

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At charged solid/liquid interfaces, electric double layers (EDLs) form with mobile ions screening the charge in the solid phase. Surface transport (ST) refers to the movement of ions present in EDLs tangentially along the solid surface (S.S. Dukhin, R. Zimmermann, and C. Werner, 2001). The latter phenomenon has been studied for decades in systems with dielectric media (S.S. Dukhin, R. Zimmermann, and C. Werner, 2001) (Thomas A. Zangle, Ali Mani, and Juan G. Santiago, 2009) (Matthew E. Suss, Ali Mani, Thomas A. Zangle, and Juan G. Santiago, 2011). Recently, the phenomenon of ST driven by applied electric fields has been studied in charging porous electrodes in the context of charge (energy) storage in supercapacitor systems (Mohammad Mirzadeh, Frederic Gibou, and Todd M. Squires, 2014). One of the conclusions of (Mohammad Mirzadeh, Frederic Gibou, and Todd M. Squires, 2014) is that including ST phenomenon in theoretical models predicts faster electrode charging. In the current work we present the effects of ST in charging porous electrodes on charge and salt dynamics during water desalination in a capacitive deionization (CDI) cell.

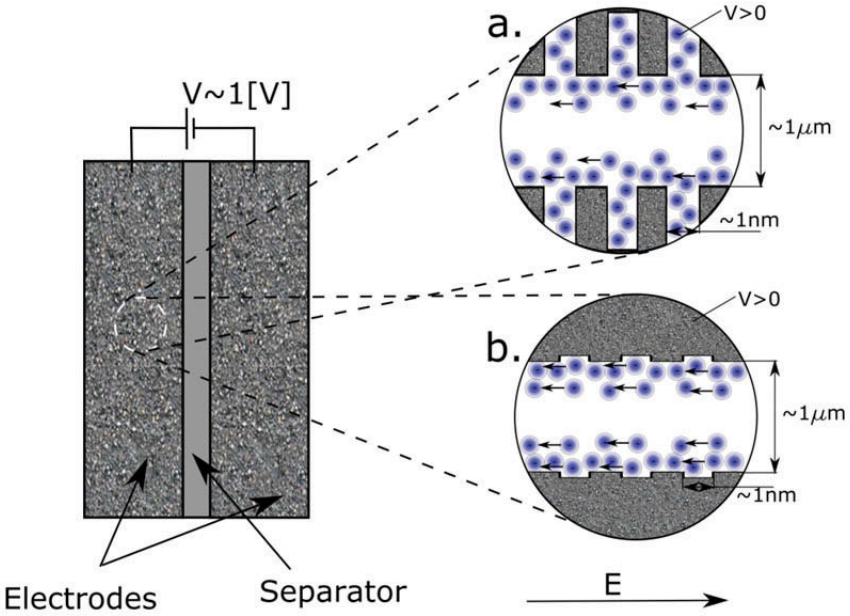

Figure 1: Schematic description of the model system. Counter-ions (the blue circles) are stored in electric double layers (EDLs) in the micropores (order 1 nm size pores) and along macropore walls (order 1 μm size pores). Under the influence of the applied electric field, E, ions can be electrosorbed into EDLs and can also move tangentially to the applied field (surface transport). Two limiting cases of a) very long and b) very short micropores are investigated.

We first analyzed the case of a porous electrode with a network of micron-scale macropores with a Gouy-Chapman (GC) EDL model. Here, we extend the Mirzadeh-Squires (MS) model by including a separator space in the domain and applying boundary conditions appropriate for CDI systems, such as a stagnant diffusion layer (Figure 2a) and that of a quiescent electrolyte, symmetric CDI cell (Figure 2b) (Mohammad Mirzadeh, Frederic Gibou, and Todd M. Squires, 2014). These two models are compared to the Biesheuval-Bazant (BB) model, which does not include the effect of surface transport (P.M. Biesheuvel, M.Z. Bazant, 2010). Our results show that for the case of a stagnant diffusion layer, the effect of surface transport speeds up the electrode charging process, similarly to the effect reported in (Mohammad Mirzadeh, Frederic Gibou, and Todd M. Squires, 2014). However for the case of the charging of a symmetric CDI cell with a quiescent electrolyte, our model shows the counterintuitive results that surface transport slows down the electrode charging. These results can be explained by the lower concentrations in the separator when including surface transport, which lead to lower local ionic conductivity, slowing down the charging process. Other results we will present will include an analysis of the case of electrodes with multi-scale pore structure, including through-electrode network of macropores and in-network micropores, as shown in Figure 1. In order to model the EDL in the electrode presented in Figure 1 we used Gouy-Chapman (GC) model near the macropores' surface and modified Donnan (mD) model in the micropores.

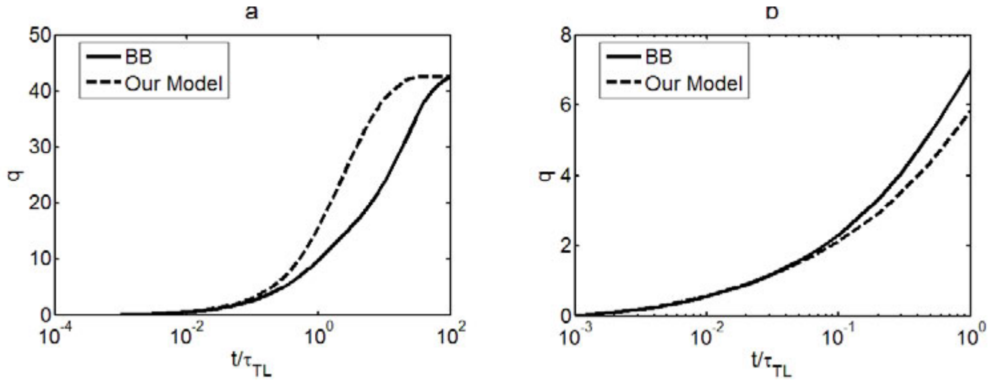

Figure 2: Results of the simulations of the effect of surface transport on CDI systems. The horizontal axis is the logarithmic, non-dimensional time scaled by τ_{TL} (the characteristic time for charging of a porous electrode when using a transmission-line model) (Mohammad Mirzadeh, Frederic Gibou, and Todd M. Squires, 2014). The vertical axis is the line-averaged excess charge density in the electrodes. The solid line refers to the model by Biesheuvel and Bazant (BB), while the dashed line refers to our model including the effect of surface transport. (a) simulates a CDI electrode with an adjacent SDL. (b) simulates a symmetric CDI cell with quiescent electrolyte.

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O7-3

MULTI-IONIC EFFECTS ON THE CAPACITANCE OF POROUS CARBON ELECTRODES

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The expansion of the electric double layer (EDL) of charged electrodes in contact with a solution, which occurs upon salinity exchange is the main concept underlying capacitive energy and desalination devices (1,2). Although most laboratory experiments have been carried out with simple salt solutions, realistic applications require a proper analysis of the effect of the presence of the different ionic species existing in natural waters (3). Moreover, these technologies can be extended to other water sources, like brine or waste water, for which, not only the species but also the salinity and temperature can differ substantially from that of the river or sea waters. Here we focus on the role of these quantities on the double layer expansion and try to provide and explanation on the basis of the equilibrium structure of the EDL. With this purpose, a model is presented in which the characteristics of the EDL where ions are tightly packed is taken into account. Using existing models of the equilibrium EDL accounting for finite volume of ions (3), it is possible to evaluate the variations of EDL properties when the concentrations, valences and sizes of ions are changed. Fig. 1 shows the calculated EDL differential capacitance when the ionic content is changed from 20 mM to 600 mM in two cases: solutions containing only NaCl and others containing the average amounts of Na^+, Mg^{2+}, $SO4^{2-}$, and Cl^- characteristic of natural sea waters.

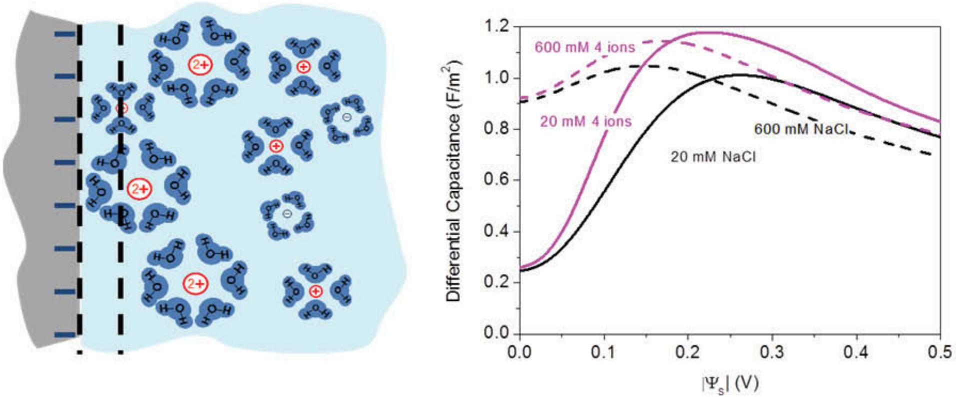

Figure 1. Schematics of the EDL in multi-ionic solutions (left) and differential EDL capaci-tance for different ionic compositions (pure NaCl and average natural sea water).

Note the different behaviours of the capacitance for both compositions tested: the presence of multivalent ions leads to an increase in capacitance (hence, lower potential for the same charge) and to smaller variations upon ionic strength changes. The latter consequence is of fundamental importance for the production of energy by salinity exchange. Fig. 2 demonstrates that this is the case, and that the energy per cycle theoretically achievable is significantly reduced if real sea water and its dilution is used in the process. In future implementations of capmix technologies, this must probably be taken into account, particularly concerning site selection. The implications for CDI will also be considered in this contribution, and the reduction of capacitive ion adsorption because of the finite volume of the ions and their exclusion by steric effects will be quantified.

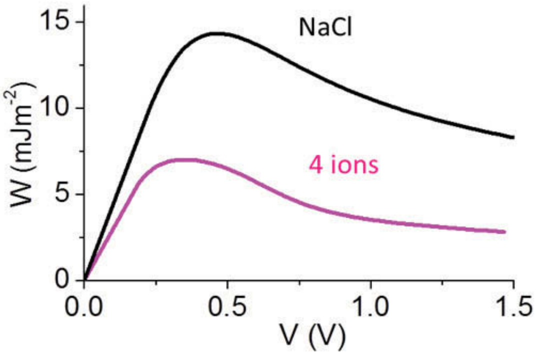

Figure 2. Energy per cycle and per unit interfacial area in a capmix salinity gradient cell for the conditions in Fig. 1.

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Acknowledgements

Financial support from MINECO, Spain, Project FIS2013-47666-C3-1-R is gratefully acknowledged.

O7-4

CDI CONTROLLED SPECTRAL EMISSION

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Although much progress has been made in light emitting devices, the ability to electrically control their spectral emission remains limited. In displays, for example, each pixel has a fixed color and only the intensity is modulated. For a tri-color display, this reduces the fill factor of each color to below 1/3. Dynamic color control may open new directions in energy saving displays, and can be expanded to a variety of different fields from controlling building's heat radiation, to dynamic clothing.

We here present the concept and preliminary results of a novel approach for dynamic color control, by electrically modulating Forster resonance energy transfer (FRET) [1] efficiency between dyes in a solution. FRET modulation is a potentially attractive control mechanism, as its efficiency depends on the 6^{th} order of the distance between donor and acceptor molecules, making it extremely sensitive to minute variations in concentrations. We hypothesize that control acceptor concentrations in a FRET cell could be achieved by using ionic molecules which would be attracted or repelled from a set of driving electrodes. Since relatively high dye-concentrations, of several percent in weight, are needed for FRET to occur, high surface area electrodes are required to yield a significant dye-concentration change in the solution, making capacitive deionization (CDI) an ideal method for this purpose.

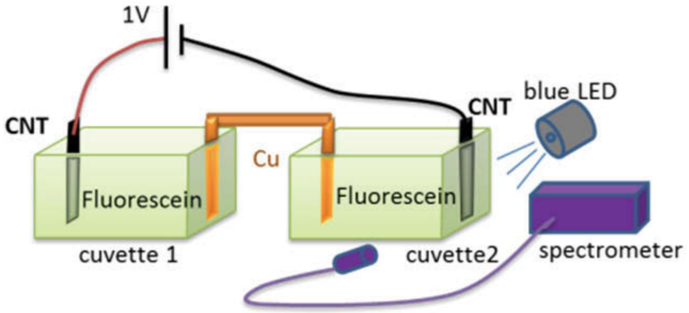

Figure 1. Schematic illustration of the experimental setup. A spectrometer measures the spectral response of a negatively charged dye contained in two cuvettes wired with a conductive metal Cu strip, and illuminated using a blue LED pump. A potential difference is applied to CNT electrodes located in each of the cuvettes.

In the present stage of the research we tested the control of a single high-concentrated charged-dye. We used Fluorescein Sodium Salt in aquatic solution, and measured its fluorescence emission modulation while applying alternating potential difference on high surface electrode, fabricated from carbon nanotubes (CNT) mats.

Activated carbon based nanostructures, such as CNT, are good candidates for high surface electrodes due to their large surface area and reasonable conductivity. However, these materials rapidly and spontaneously adsorb dyes from a solution without applying any voltage [2]. Thus, to eliminate the influence of any adsorption which is not associated with the external applied voltage, we soaked the electrodes in the dye solution for 12 hours before the experiment. Once the electrodes were fully saturated with dye, we integrated them into the experimental setup. For a single cell with two CNT electrodes, the cathode repels the negatively-charged dye contained within, while the anode attracts and adsorbs it, resulting in unchanged dye concentration in the bulk solution. To solve this issue and to detect modulation in the dye concentration, we chose a double cell setup configuration as depicted in Figure 1.

Initially we set identical dye-concentrations in both cuvettes, and thus the same fluorescence emission intensity was measured for each cell. Applying a potential of 1V DC between the CNT electrodes induces dye adsorption in the CNT electrode in cuvette 1 and dye repulsion from the electrode to the bulk in cuvette 2. Therefore decreased and increased fluorescence emissions were measured from cuvette 1 and 2, respectively, as imaged in Figure 2a. Inverting the applied voltage resulted in an opposite trend: cuvette 1 showed increased emission and cuvette 2 emission decreased.

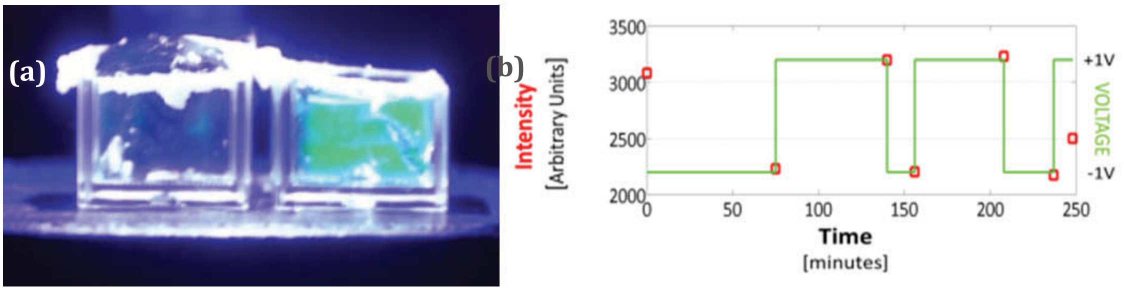

Figure 2. Experimental results: **(a)** Raw fluorescence image of the coupled cuvettes after applying 1 V for 45 minutes, showing the fluorescence in one of the cuvettes diminished, while the other intensified. **(b)** Measured intensity at the peak fluorescence wavelength, λ_{em}=515 nm (red symbols) modulated by the electrodes potential (green solid line).

To explore the repeatability and the reversibility of the process we measured three cycles; for each cycle the potential was applied until the emission intensity was changed by ~50%, and then the potential was inverted until the intensity reached its initial value. As expected, we obtained modified fluorescence intensity as we alternated the potential in each cycle (Fig. 2b).

In summary, we demonstrated experimentally the control of dye concentration. We envision that this method will open the door for implementation of dynamic color modulation, useful in various applications. Our future research focuses on a single cell device with two high surface area electrodes saturated with oppositely charged ions.

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SESSION 8: HETEROATOM CARBONS AND BEYOND

O8-1 (invited)

ENHANCED CAPACITIVE DEIONIZATION ABILITY OF NANOCARBON MATERIALS BY NITROGEN DOPING

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Due to the world's water crisis and increasingly severe pollution around the globe our world is in badly need of efficient and environmentally friendly water treatment technologies. As a brand new technology of water treatment, CDI has shown great potential due to its high efficiency and energy conservation over conventional deionization technologies such as evaporation, reverse osmosis, and electrodialysis. This technology is proceeded through adsorbing ions into the electric double layer formed at the surface of electrodes when a low direct current potential is applied. This principle of CDI makes it an environmentally-friendly process with good reversibility.

Engineering of carbon materials by substituting some of the carbon atoms with heteroatoms, such as nitrogen, phosphorus, boron and so on, is an effective way to modify their electron transfer properties,[1-3] and ultimately improve their electrical and chemical performance. Among numerous heteroatoms, nitrogen is the most potential candidate as its atomic size and valence bond are both similar to those of carbon atoms.[4-6] Doping of nitrogen atoms into graphitic networks is considered to be one of the best approaches to produce materials with improved conductivity.[7-11] Moreover, nitrogen-doping can induce a large number of defects in the carbon nano-structure.[12, 13] The presence of defects can generate more accessible surface area and cause an increase in ability for the accumulation of charges, which is beneficial to the charge transfer.

In this review, nitrogen-doped carbon materials, including graphene, carbon nanofibers, carbon sphere, graphene sponge, etc., for CDI applications are systematically presented. Applications of these nitrogen-doped carbon materials for the removal of the salt ions from solution are demonstrated to be highly effective and they exhibit improved CDI performance compared with pristine carbon electrodes.

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O8-2

CAPACITIVE DEIONIZATION USING BIOMASS-BASED MICROPOROUS SALT-TEMPLATED HETEROATOM-DOPED CARBONS

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Capacitive deionization (CDI) is an ion removal technology primarily designed for treatment of aqueous electrolytes such as brackish water. Upon applying a voltage difference between the two chemically unmodified porous carbon electrodes separated by a spacer channel, cations are stored in the cathode and vice-versa for the anions [1,2].

Microporous carbons are an interesting material for electrochemical applications. In this study, we evaluate several such carbons without/with N or S doping with regard to capacitive deionization. For this purpose, we extent the salt-templating synthesis towards biomass precursors and S-doped microporous carbons [3]. The sample with the largest specific surface area showed 1.0 wt% N and exhibited a high saltsorption capacity of 15.0 mg/g at 1.2 V in 5mM aqueous NaCl [4]. While being a promising material from an equilibrium performance point of view, our study also gives first insights to practical limitations of heteroatom-doped carbon materials. We show that high heteroatom content may be associated with a low charge efficiency [4]. The latter is a key parameter for capacitive deionization and is defined as the ratio between the amounts of removed salt molecules and electrical charge.

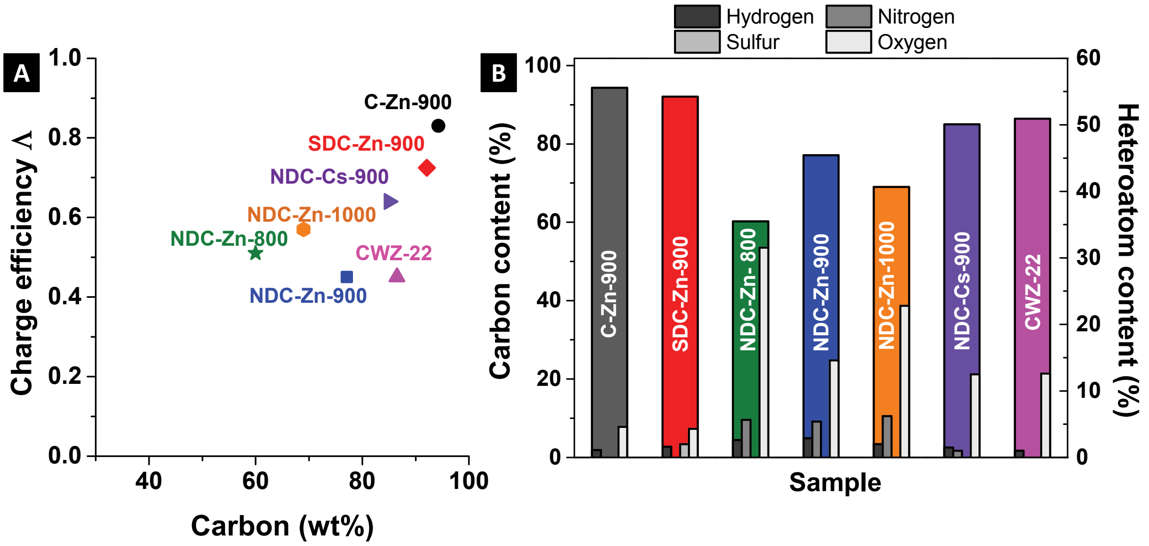

Fig. 1 A) Relation between charge efficiency at c_{salt}=5 mM and V_{cell}=1.2 V for all carbon electrodes tested in CDI as function of C content. B) Chemical analysis of the carbon samples tested in CDI.

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O8-3

NITROGEN-DOPED CARBON AEROGELS FOR CAPACITIVE DEIONIZATION

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Capacitive deionization (CDI) is a potential method to remove ions from aqueous solution due to its less energy consumption and capital intensive.[1] The electrosorption performance is strongly dependent on the properties of the electrode materials. Owing to the good chemical stability and cost consideration, carbon-based materials are one of the candidates for CDI progress. Carbon materials are usually featured by inert surface, thus heteroatom (N, O, S, B) substituted for carbon in carbon-based materials as active sites can modify the electronic properties, which can further influence the electrochemical performance of carbon-based material. We have synthesised the nitrogen-doped carbon aerogels through a facile polycondensation reaction catalyzed by Na_2CO_3 under ambient pressure drying. The samples were identified as CA, CAN-0.2, CAN-0.3 and CAN-0.6, according to the different mass ratio of M:R in the carbon aerogels. Introduced nitrogen into the carbon frame enhances the surface wettability which benefits for the electrolyte ions into the inner layer of the carbon aerogels. The preparation process of the nitrogen-doped carbon aerogels is illustrated in Fig. 1.

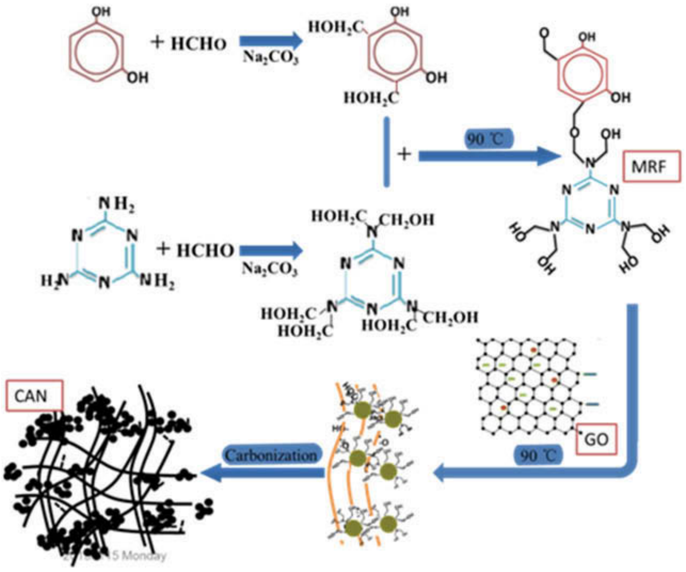

Fig. 1. Schematic illustration of preparation process of nitrogen-doped carbon aerogels

Fig. 2 and Table 1 present the data of CAN-0.6 at the voltage of 1.6 V and at a direct current of 15 mA, 20 mA and 25 mA with concentration of 800 mg L^{-1} from adsorption capacity and energy consumption in the CDI operation. It shows that the energy consumption of per milligram salt removed at a constant electric current is lower than that at a constant voltage in CDI operation. The reason for this phenomenon is that the extra applied constant electron current translates into an equally large ionic current in the CDI-operation, which has contributions from the ionic flux of positive ions (Na^+) and negative ions (Cl^-).[2,3] These results suggest that CANs have a potential application in CDI process at a constant current operation due to its lower cost and higher electrosorption performance.

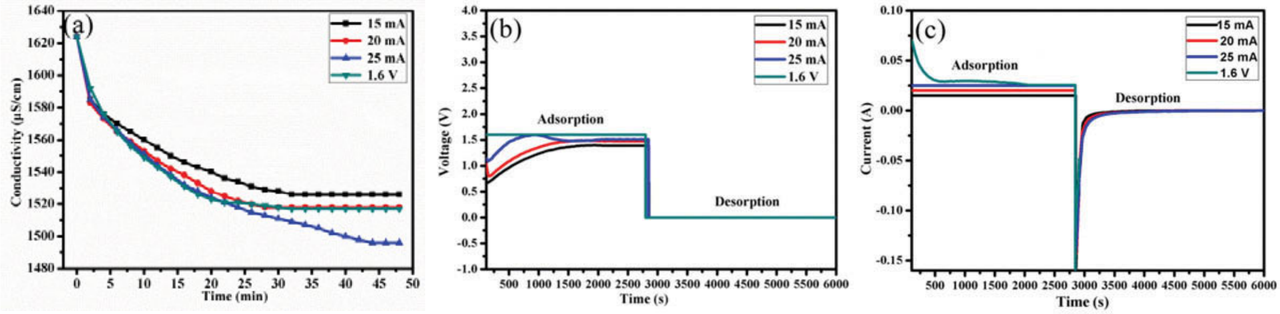

Fig. 2. The comparison of CC and CV in CDI-operation: (a) Electrosorption of NaCl on CAN-0.6; (b) Voltage-time curves; (c) Current-time curves.

Table 1. The comparison of electorsorption capacity and energy consumption.

Test conditions	Charge Energy ($J\ g^{-1}$)	Adsorption capacity ($mg\ g^{-1}$)	Energy consumption ($J\ mg^{-1}$)
15 mA	46.05	12.23	3.765
20 mA	68.08	14.48	4.702
25 mA	87.22	16.72	5.461
1.6 V	101.19	13.35	7.580

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O8-4

PSEUDOCAPACITIVE ELECTROSORPTION OF CARBON DIOXIDE AND OTHER ACID GASES

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We explore the use of asymmetric supercapacitor membrane assemblies of novel architecture for the electrosorption and subsequent release of carbon dioxide and other acid gases. The electrodes rely on Faradaic pseudocapacitance in which the gas uptake and release are regulated by changes in the affinity of a functional group based on changes in the redox state of the material. We will discuss the preparation of the electrodes, including their chemical synthesis and assembly into the working cell; the electrochemical characterization of the electrode assembly; and the dynamic uptake and release of the targeted compounds under a range of different operating conditions, including both batch and cyclic continuous flow systems. The talk will conclude with an evaluation of the concept for a number of different applications, a discussion on the dynamics and energetics of the process, and an assessment of enhancements that can be made in the process.

SESSION 9: MCDI

O9-1 (invited)

ION TRANSPORT THROUGH ION EXCHANGE MEMBRANES

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Ion transport through ion exchange membranes is an essential element of efficient CDI devices. This contribution presents a variety of different works developed over the years on this intricate matter.

First it presents means to tailor the monovalent/bivalent ion selectivity by applying a controlled layer-by-layer surface architecture [1].

Secondly, it presents a comprehensive model describing ion transport of multi-ionic solutions through layered electrolyte and polyelectrolyte structures [2]. The new direct numerical simulation model is coined E*n*PE*n*: it allows to solve a set of first principle equations to predict for multiple ions their concentration and electrical potential profiles in electro-chemically complex architectures of *n* layered electrolytes E and *n* polyelectrolytes PE. E*n*PE*n* can robustly capture ion transport in sub- millimeter architectures with submicron polyelectrolyte layers. E*n*PE*n* captures yet unsolved architectures such as (a) selective Na over Ca transport in surface modified ion selective membranes and (b) transport of weak electrolytes.

In a third part, the presentation focuses on ion transport above the limiting current density. In particular it addresses the onset of an electro-kinetic instability coined electro-convection. First, the earlier demonstrated experimental proof is reviewed [3] and then an early trigger of electroconvection is suggested [4].

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O9-2

MODELING ION-EXCHANGE MEMBRANE TRANSPORT FOR ENERGY HARVESTING AND DESALINATION

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Ion exchange membranes (IEMs) are widely used in several industrial applications, ranging from conventional separation (e.g., electrodialysis, ED) to energy generation (reverse electrodialysis, RED [1]). Novel applications of IEMs are in membrane capacitive deionization (MCDI).

A full understanding of the ion transport phenomena involved in these processes requires the description of both the convective flux along the compartments and the electro-migrative flux towards and through the membranes.

Up to now, a number of modeling approaches have been reported in the literature, based either on the Nernst-Planck equation or Stefan-Maxwell theory [2]. Despite much progress, most of the modeling works are based on strong simplifying assumptions, e.g., the use of the concept of the Nernst diffusion layer. Moreover, such models usually make use of membrane parameters such as transport number or permselectivity as input. In fact, permselectivity and transport numbers are ideally outputs of a proper model, not inputs. Thus, there is still a lack of a comprehensive model describing the fundamental aspects of IEM transport processes.

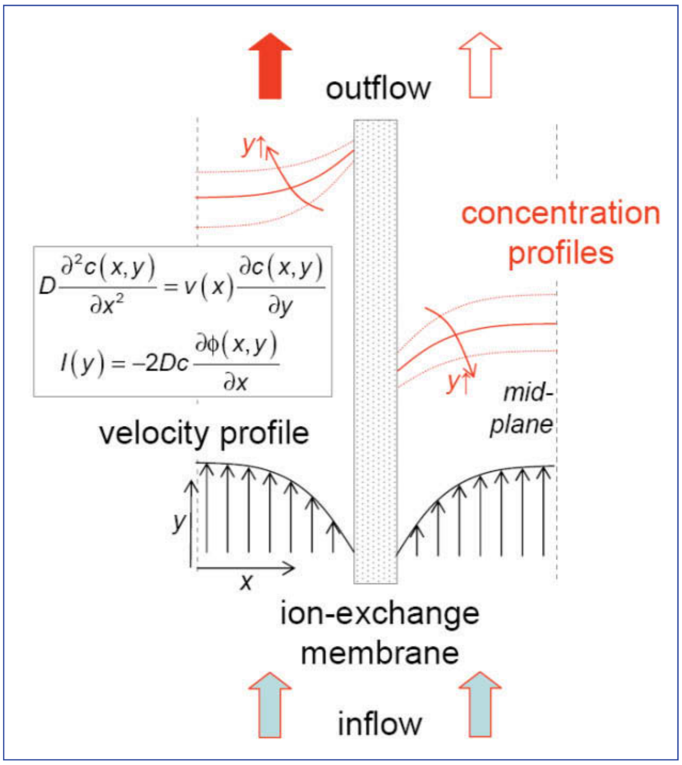

Fig. 1. Simplified scheme of the 2D transport model under ED mode. The system consists of a concentrate compartment, an ion exchange membrane, and a diluate compartment.

In this work, a simple 2D model is proposed based on the work of Sonin and Probstein [3], where the Nernst-Planck equation describes the ions transport both in the solution and through the membranes (Fig. 1). We extend the work in ref. [3] by considering non-ideal membranes that allow transport of both counter- and co-ions.

The model accurately estimates the voltage profile arising across the cell, due to the formation of a Donnan potential at each membrane-solution interface [4-5]. In this way, it is able to predict correctly the membrane behavior in a wide range of process conditions, accounting for electrodialysis (ED), reverse electrodialysis (RED) and MCDI.

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O9-3

QUANTITATIVE ANALYSIS OF MECHANISMS OF ION-EXCHANGE RESIN-COATED CAPACITIVE DEIONIZATION

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Capacitive deionization (CDI) is an emerging desalination technology based on electrochemical principles that ions are adsorbed onto the electrode surface where potential is applied. Membrane capacitive deionization (MCDI) is a modified system by inserting ion-exchange membranes (IEMs) in front of the carbon electrode and shows higher desalination performance than CDI.

However, the expensive IEMs significantly lower competiveness of CDI over other technologies. So there are many attempts to substitute membranes with another material. One of the alternatives are ion-exchange resins (IERs). The resins can be coated onto the carbon electrode and form low-cost thin film (Kim et al., 2010). The CDI system assembled with the coated electrodes were referred as SCDI. SCDI demonstrated higher desalination performance than pristine CDI and even showed comparable performance to MCDI. However, role of IERs in such improved performance are not yet clear.

Therefore, in this research, we investigated performance of SCDI by using a mechanism of MCDI. We expected both IEM and IER would behave under similar principle. For that purpose, experiments were conducted with activated carbons that have similar BET specific surface area but different micropore/mesopore ratio. As a result, we examined that MCDI mechanism could also be applicable to explain the enhanced performance of SCDI.

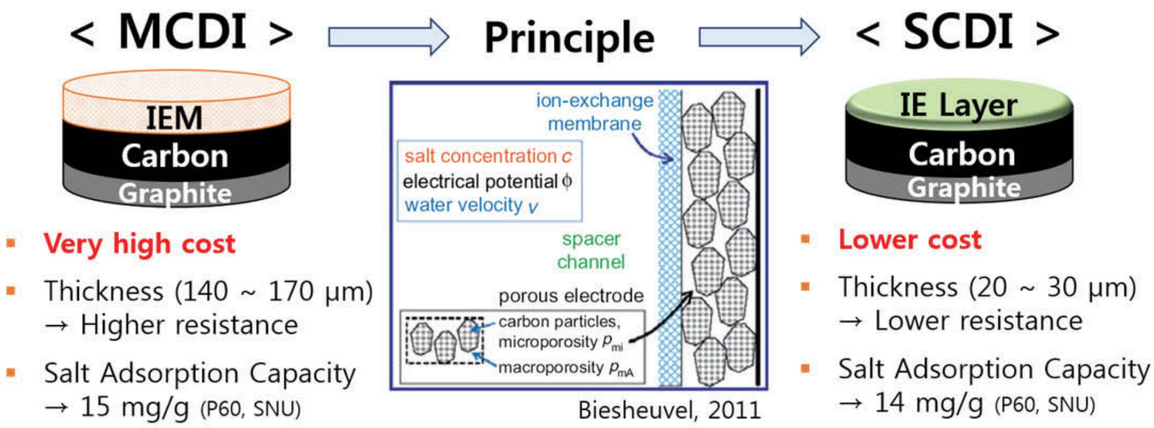

Fig. 1 Comparison between MCDI and SCDI which have advantages in cost and thickness compared to MCDI. Both systems seem to share the same principle.

O9-4

ADVANCED FULL SCALE MEMBRANE CAPACITIVE DEIONIZATION SYSTEM FOR RIVER WATER TREATMENT

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Voltea's patented Membrane Capacitive Deionization MCDI is an electrochemical technology designed to deionize water up to approximately 8000 ppm total dissolved solids. Key advantages of Voltea's technology are low energy consumption and high water recovery. In MCDI ions are removed from feed water by applying an electrical potential difference between two electrodes covered with ion exchange membranes. Electrodes are separated from each other by a spacer, whereby water flows and the ions are removed from the feed water. These ions are temporarily stored in the electrical double layers, which are formed at the electrode interface. When the electrodes become saturated with ions, they are regenerated by reversing the applied voltage and/or short circuiting. After the ions have been released from the electrodes, a waste stream is produced and captured ions are flushed from the module.

We would like to present the biggest and the most advanced full scale MCDI installation in the world. This system is designed to treat river water (Black river, Ohio, USA) which produces 300m^3 of water per day at 72% water recovery. Energy consumption for this installation is 0.42kWh/m3 for produced water which is approximately half when compared to reverse osmosis. As a point of note the composition of the Black River water changes significantly with seasonal variations and weather effects. This poor water quality would not allow use of RO technology without significant pre-filtration. Voltea's MCDI employed a simplistic, low cost, low maintenence multimedia filter for its pre-filtration. To counteract the season water quality changes Voltea employs our smart dynamic control system which ensures that the produced water has a constant quality independent of the incoming water composition. Our MCDI system is also equipped with fully automated smart cleaning-in-place system which ensures that modules are kept clean without constant operator intervention as with other membrane technologies. In addition, we would like to present new applications for MCDI technology, such as but not limited to: commercial laundry, agriculture, point-of-entry and appliance water softening, controlling cooling towers, surface and waste water treatment.

O9-5

ASYMMETRIC MEMBRANE CAPACITIVE DEIONIZATION WITH ECO-FRIENDLY CATION EXCHANGE MEDIA COATED-CARBON ELECTRODE FOR HARDNESS CONTROL

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Hard water minerals in drinking and industrial water cause problems such as pipeline scaling and membrane fouling. Also the minerals can react with soap anions to reduce cleaning effect of water. Capacitive deionization (CDI) can be a cheap and low-energy consuming alternative that electrostatically remove hardness ion species in the water. Membrane-assisted CDI (MCDI) were introduced to improve the performance of pristine CDI. Although the charge efficiency and the desalination performance of CDI were greatly enhanced, the expensive ion-exchange membrane remains as a challenge to commercialization. Many researches are conducted to invent membrane-less system or to develop low-cost and environmentally benign membranes.

Calcium alginate, an extract from sea weed, is widely used in pharmaceutical, food-industry, and water treatment as a cost effective and eco-friendly polymer gel. Calcium alginate is a gel structure that is formed via calcium substitution reaction. This gel exhibits excellent hydrophilic and also ion-exchangeable properties.

In our research, we for the first time, introduce calcium alginate (Ca-Alginate) as a cation exchange resin in CDI. The polymer resin was coated on a negative carbon electrode and CDI module was assembled asymmetrically with anion-exchange membrane on the positive electrode. The Ca-Alginate asymmetric MCDI system (CA-MCDI) was compared with pristine CDI and conventional MCDI with commercial ion exchange membranes. The CA-MCDI system demonstrated greater desalination performance than pristine CDI and even comparable result with conventional MCDI as shown in Figure 1 (a) below. Moreover, CA-MCDI exhibited highest charge efficiency among the CDI systems as Figure 1 (b) shows. We have successfully demonstrated potential usage of eco-friendly Ca-alginate polymer resin as an alternative to costly commercial cation exchange membrane in CDI process.

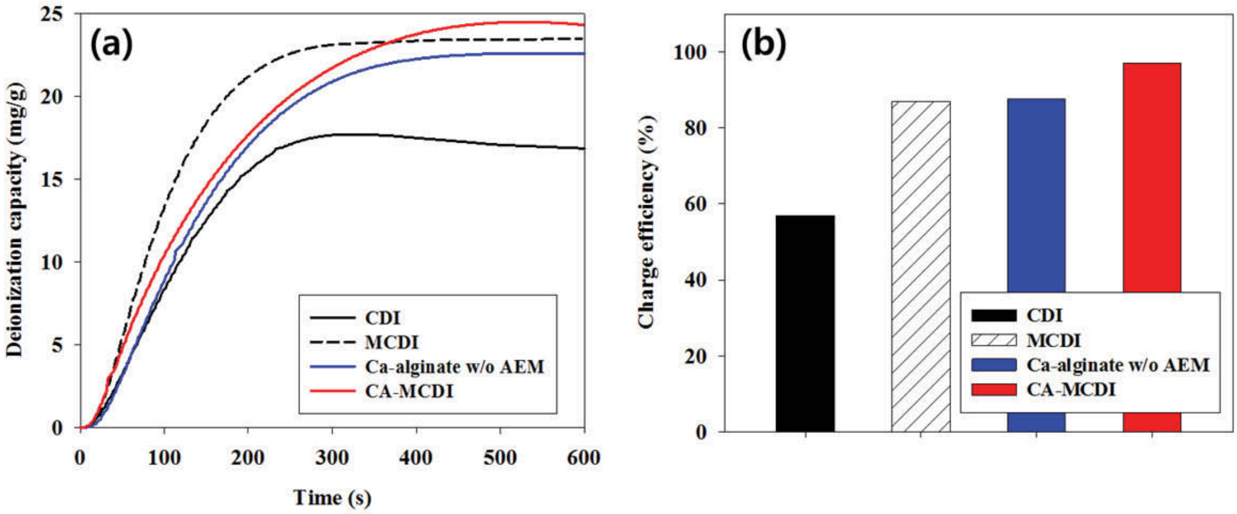

Figure 1. (a) Deionization capacity and (b) charge efficiency of the four CDI systems: CDI, MCDI, CA-MCDI without AEM, and CA-MCDI.

SESSION 10: MCDI

O10-1 (invited)

RESEARCH ON ELECTRODES AND ION EXCHANGE MEMBRANES IN CAPACITIVE DEIONIZATION

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Electrodes made of graphene laminates (GL) with favorable electrochemical properties were used to remove sodium and ammonium ions by membrane capacitive deionization (MCDI). First, the electrosorption mechanisms of the GL-based electrodes were investigated by adsorption isotherms, kinetic models and thermodynamics under different concentrations of aqueous sodium chloride (NaCl). The ion sorption followed the Langmuir isotherm corresponding to monolayer adsorption and indicated a physicsorption process according to thermodynamic parameters. The GL-based electrodes were then used to remove ammonium chloride (NH4Cl). With an initial concentration of 400 mg/L, the NH4Cl removal capacity was 15.3 mg/g at 20 ºC with a removal efficiency of 99%, indicating similar electrosorption characteristics to NaCl. A higher removal rate of ammonium ions was demonstrated compared to that of sodium, confirming that the GL-based capacitive deionization (CDI) process can effectively remove ammonium ions from aqueous solutions.

Ion exchange membranes used in the electrosorptive water purification process such as capacitive deionization (CDI) is required not only have high ion exchange capacity but also have good electrical conductivity to minimize the electrical resistance. One of the problems of available ion exchange membrane (IEM) is lack of high electrical conductivity. In this study, a series of novel more conductive anion exchange membranes were prepared by dry phase inversion method, where the reduced graphene oxide/polyaniline (RGO/PANI) was added in the polyvinydene fluoride (PVDF) polymer matrix. The prepared membranes possess both higher electrical conductivity and high ion exchange capacity (IEC). By adding RGO in the membrane solution, it allowed higher PANI loading (for up to 50% PANI) in the PVDF solution. It was found that the water content of the prepared membranes can be controlled by balancing the added RGO and hydrophilic material PANI in the polymer matrix, this strategy can avoid the water content becoming too high. The electrical conductivity of the samples added with RGO all showed significantly improvement; with the conductivity values were more than doubled against the one without RGO. More importantly, it was found that adding the RGO/PANI in the membranes formula has increased the salt removal efficiency and sorption capacity. It was found that sample LG 50, with low GO concentration, and 50% PANI/RGO composites in the membrane showed the best performance among all the membranes prepared.The results from this work lead to a better understanding of the relationships between conductivity and IEC, water content and transport number, which help to develop more efficient anion-exchange membranes for CDI and other water related applications.

O10-2

ION EXCHANGE SPACER MATERIALS FOR ENHANCED DESALINATION RATE AND CHARGE EFFICIENCY IN CAPACITIVE DEIONIZATION

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In addition to a high salt adsorption capacity (SAC), performant and cost-effective CDI cells also need to have a high salt adsorption rate (SAR). The ionic transport resistance of the spacer section of a CDI cell can be a significant factor determining the SAR, particularly for low salinity applications. We report on the enhancement of the SAR and of the charge efficiency by substituting conventional spacer material with materials that contain a fixed chemical charge, in a flow-between activated carbon electrode capacitive deionization cell operated in constant voltage mode (1.2 V).

A single layer of pre-saturated monodisperse (500 µm) cation exchange beads (CEB) or of anion exchange beads (AEB) was used. Respectively, the charge densities of these two bead layers were 1.9 eq/dm^3 and 1.0 eq/dm^3. For a 5 mM NaCl influent, this resulted in a maximal instantaneous SAR of 1.38 mg/g/min for CEB and 1.02 mg/g/min for AEB, which is 2.1 and 1.5 times higher than for the CDI cell containing a relatively thinner (300 µm), conventional glass fiber spacer (fig. 1). Improving the desalination rate of a CDI cell allows one to operate the system at shorter half-cycle times (HCT). For the shortest tested HCT of 200 s, the average salt adsorption rate (ASAR) was 1.2 mg/g/min for CEB and 0.7 mg/g/min for AEB, an improvement by a factor of respectively 6.0 and 3.5 (fig. 2). Although operating at a short HCT typically leads to a decrease in the charge efficiency, the use of ion conductive spacers was found to significantly mitigate this (fig. 2). An HCT of 200 s or 500 s results in a low charge efficiency of respectively 17% and 49% for the glass fiber spacer case, whereas for CEB spacers the charge efficiency was 53% at 200 s and at 500 s there was no significant difference compared to the equilibrium HCT.

We will also show similar results for a 20 mM influent and for a spacer consisting of a mixture of anion and cation exchange beads, as well as for one consisting of beads with no fixed charge.

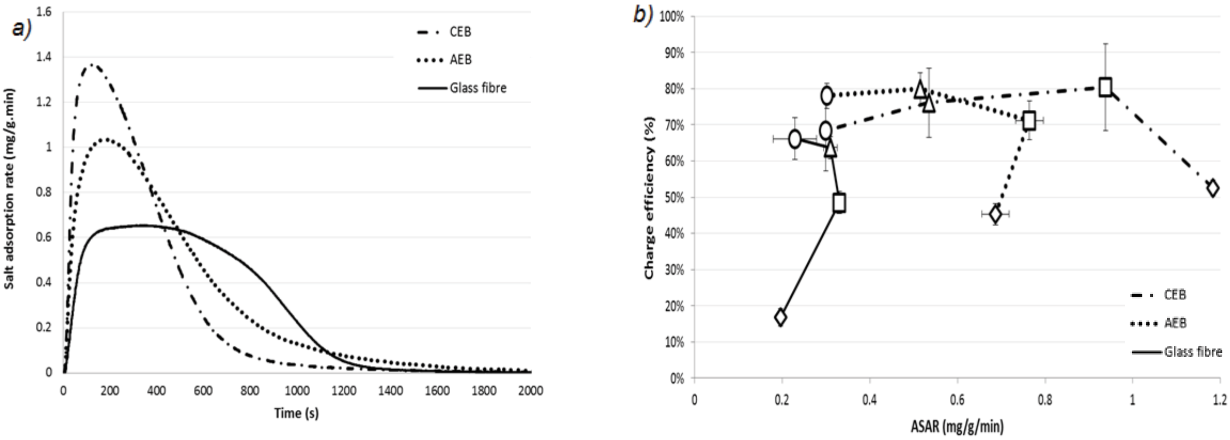

Figure 1: a) Salt adsorption rate as a function of time during a constant voltage adsorption half cycle using a glass fiber spacer, anion exchange bead spacer (AEB), resp. cation exchange bead spacer (CEB). b) Charge efficiency vs average salt adsorption rate during constant voltage adsorption half cycles with duration 200 s (◇), 500 s (□), 1000 s (△) and 1800 s (○).

O10-3

CAPACITIVE SEPARATORS FOR ENHANCED DESALINATION PERFORMANCE OF MEMBRANE CAPACITIVE DEIONIZAITON

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Membrane capacitive deionization (MCDI) is considered to be a competitive technology for desalination. In MCDI, ions migrate from aqueous solution, across the ion exchange membranes and then stored on the surface of electrodes. Although it remains unknown which represents the rate-limiting step, strengthening ion transport/migration in the bulk solution is, no doubt, beneficial for facilitating the desalination performance.

To accelerate desalination rate in flow channel, a new design of membrane capacitive deionization (MCDI) cell was constructed by packing the cell's flow chamber with granular activated carbon (GAC) (Fig.1 A). When the distance of membranes was 2 cm, the GAC packed-MCDI (GAC-MCDI) delivered higher (1.2–2.5 times) desalination rates than the regular MCDI (unpacked MCDI) at all test NaCl concentrations (~100–1,000 mg/L) (Fig.1 B). Comparatively, packing the MCDI's flow chamber with glass beads (GB; non-conductive) and graphite granules (GG; conductive but with lower capacitance than GAC) resulted in inferior desalination performance. We attribute the better performance of GAC to the electric double layer (EDL) formed on the surface. The higher surface conductivity than that of in bulk solution could reduce ionic resistance and thereby enhancing the MCDI's desalination rate.

Based on the enhanced desalination rate of MCDI packed with GAC above, the separator of MCDI was optimized by using activated carbon fibre (ACF) (membrane distance was 0.5 mm). The highest desalination rate was obtained in MCDI with ACF as separator, which was 37% higher than that with stainless steel fibre separator and 72% higher than that with filter paper separator. Our results highlight the need to develop separators that facilitate ion transfer in flow channel of MCDI.

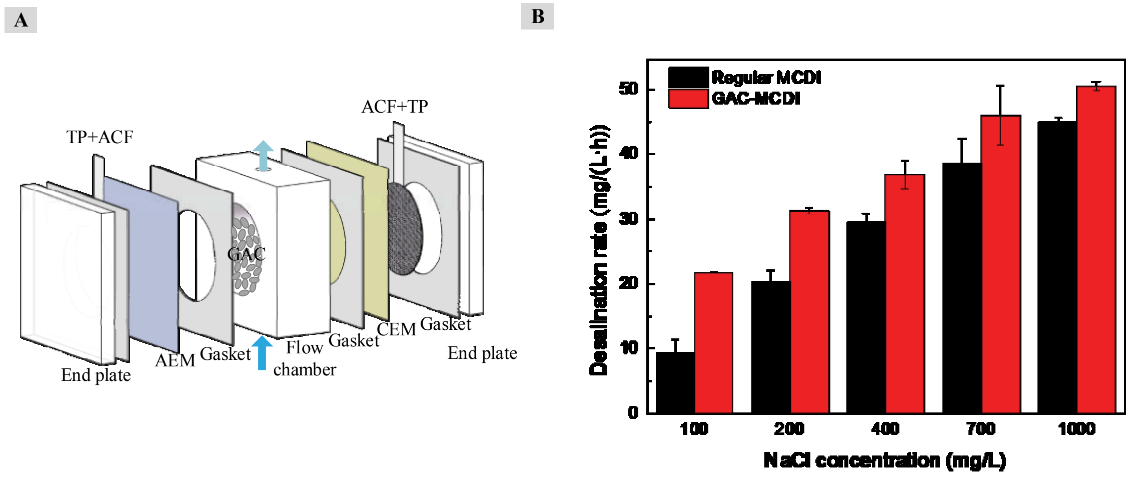

Fig.1 (A) Schematic diagram of membrane capacitive deionization (MCDI) cell. (B) Desalination rates of regular MCDI vs a GAC-MCDI cell at different initial NaCl concentration, for which the test conditions are Vcell:1.2 V, V NaCl: 30 mL

O10-4

A NEW CONTINUOUS METHOD TO DESALINATE SALT WATER

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Recently, a new method of desalination by CDI, called flow electrode capacitive deionization (FCDI), has been developed which utilizes a flowing carbon slurry electrode to electrosorb salts. Compared to traditional CDI, FCDI enables continuous desalination and the treatment of higher salinity feedwaters.[1] However, flow electrodes suffer from low electronic connectivity (high electronic resistance) due to a low maximum carbon mass percent in the flow electrode (typically ~25% or less), and also high flow electrode viscosity resulting in parasitic pump losses.[2, 3] We here present a new method to desalinate salt water via electrodes with carbon suspensions which can overcome these limitations, which we term “fluidized bed CDI” (Fbed CDI). Fluidized beds are widely used in chemical reactors and combustion processes, and these use the flow of a suspension of carbon beads against the direction of gravity. The latter results in a densely packed fluidized bed, where the carbon beads travel more slowly than the surrounding water (see Figure 1). Fbed CDI leverages an upflow (or moving), liquid-solid fluidized bed to enable a highly dense (mass percent up to 55% or particle volume percent up to 75%) bed of carbon beads formed uniquely inside the electrode suspension compartment. While a dense bed is formed in the electrode compartment, the mass loading of carbon in the tubings and tank outside the cell remains low (< 10%), limiting pump losses. We here also show the results of a continuous desalination process using our Fbed CDI system, where the system used only one desalination cell and one electrode tank where beads are regenerated during operation (see Figure 2).

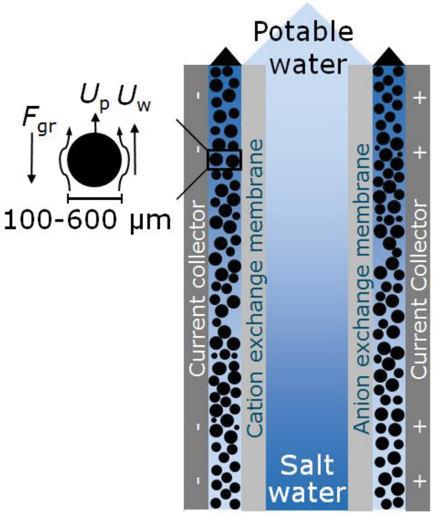

Figure 1: A schematic of the Fbed CDI system presented in this work. Flow is upwards (against gravity), allowing for fluidization of the flowing activated carbon beads

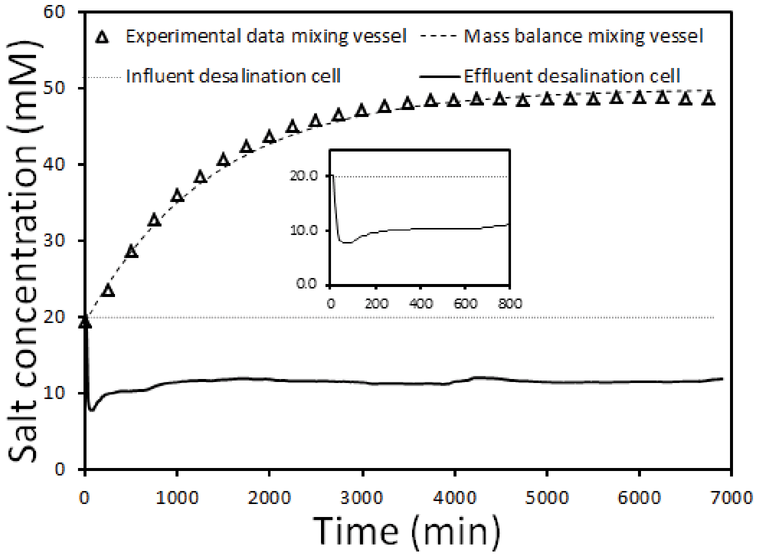

Figure 2: Desalination results demonstrating continuous desalination of the feedwater. Cell voltage applied was 1.6 V, and the electrolyte was 20 mM NaCl. The cell effluent is shown by a solid line, and the approach to steady state of the brine tank by a dashed line. The feedwater concentration is shown by the dotted line. Inset shows the early time dynamics of the effluent concentration upon applying the cell voltage.

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POSTER PRESENTATIONS

P-1

MODELLING AND CONTROL OF TRAVELLING WAVE CAPACITIVE DEIONIZATION DESALINATION SYSTEM

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This paper discusses a novel approach of modelling and control of capacitive deionization water desalination system using the concept of travelling electric wave. Three CDI cells consisting of electrodes with high surface area are connected in series wherein a moving electric field in the first cell separates the salt ions by adsorption of cations to the cathode and anions to the anode, further forcing the cations and anions from the first CDI cell to move to a second cell and finally to the third one. The flow out of the first cell has a substantially less total dissolved salt (TDS) than the inlet flow to the cell. The fraction of the produced low salt water, called reflex, is recombined with the inlet salty water for controlling the amount of salt in the produced fresh water. The cations and anions are finally accumulated in the third CDI cell at the respective electrode terminals and are later combined and discharged as brine. The reflex flow rate is adjusted to regulate the salt contents in the produced fresh water at a desired concentration, while the brine flow rate is adjusted to achieve an economical water recovery ratio.

P-2

ACTIVATED CARBON FOR THE ELECTROSORPTION OF TRIVALENT CHROMIUM

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Capacitive deionization permits the removal of ions using a very low energy. The challenge is focused then in the design of electrodes able to reach the major quantity of removal of ions, reason why each time new materials are made and tested to this goal. In this work, activated carbon has been utilized as electrode to remove trivalent chromium, since this material is known for its good adsorption capabilities for adsorption of not only ions, but organic compounds and gases. The tests were designed to evaluate the capability of the activated carbon to remove Cr (III) as adsorbent and then as electrode in an electrosorption process. Isotherms, dosage and kinetics were done for study the adsorption phenomena and experiments of isotherms and kinetics were run for study the electrosorption process. The trivalent chromium was considerate as problem ion due to its presence in tanning process, potential source of pollution by itself and possible oxidation to Cr (VI), becoming toxic.

Activated carbon itself showed a capacity to remove Cr (III) as 17 mg g^{-1}, obtained from Langmuir isotherm and a time to remove all the ions from 100 ppm Cr (III) 100 mL solution of 2.5 h, meanwhile the time were diminished using electrosorption system.

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P-3

ACTIVATED CARBON ELECTRODES WITH IMPROVED CHARGE STORAGE CAPACITY AND CAPACITIVE DEIONIZATION PERFORMANCE

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Activated carbons (AC) are the most commonly used electrode material for capacitive applications, such as supercapacitors or capacitive deionization (CDI).[1-3] This is well explained by their suitable electrical conductivity, high specific surface area, and moderate/low cost considering the high availability of renewable carbon sources. The porosity is of particular importance for CDI, because the salt adsorption capacity (SAC) is limited by the ion accessible total pore volume. Thus, in an ideal system, an increase of the pore volume of AC should also increase the SAC.

There exist various techniques and strategies to maximize the pore volume of CDI electrode materials.[4] From an application point of view, the activation of commercially available AC materials is of special interest. In our study, we used commercially available YP80 (Kuraray) AC and applied an easy-to-scale and facile-to-apply physical activation method via CO_2 treatment at temperatures between 950 °C and 1020 °C. While the pore volume and surface area can be significantly increased from 1.07 cm^3/g and 1786 m^2/g up to 1.51 cm^3/g and 2113 m^2/g, this comes at the expense of making the carbon more hydrophobic giving electrodes with water contact angle of 120 °and with significantly lowered electrode density from 0.44 g/cm^3 to 0.33 g/cm^3.

To overcome this limitation, we present a novel strategy to still capitalize the improved pore structure by admixing as received (more hydrophilic) carbon with CO_2 treated (more hydrophobic) carbon for CDI electrodes without using membranes. Using this approach, the wettability of the electrodes was significantly improved with contact angles around 80 ° (Fig. 1A). This translates in an enhanced charge storage ability in high and low molar concentrations (1 M and 5 mM NaCl) and significantly improved CDI performance (at 5 mM NaCl). In particular, we obtain in 1 M NaCl an increase of specific capacitance from 135 F/g to 155 F/g by galvanostatic discharging at 0.1 A/g, which was much more pronounced for discharging at 10 A/g. We obtained also a stable CDI performance at 0.86 charge efficiency with 13.1 mg/g SAC for an optimized 2:1 mixture (by mass) using 5 mM deaerated NaCl at 1.2 V (Fig. 1B).

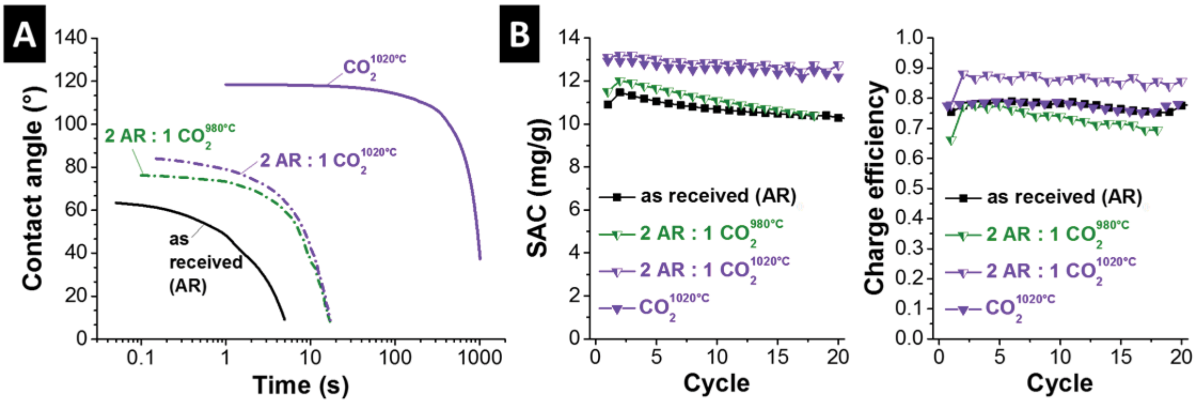

Fig. 1: (A) Time dependent water contact angle of film electrodes with different composition. (B) SAC (left) and charge efficiency (right) of different film electrodes in 5 mM NaCl at 1.2 V for 20 full cycles.

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P-4

NEUTRON SCATTERING AS A PROBE FOR ION ELECTROSORPTION IN POROUS MEDIA

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Understanding the molecular-scale behavior of ions at interfaces and under nano-confinement is crucial to describing phenomena in electrical energy storage devices and capacitive deionisation and electrosorption technologies. In supercapacitors, which are devices that store energy via the reversible electrosorption of ions on a high surface area electrode, the highly porous, high surface area networks of the electrode materials introduce nano-confinement and surface effects on the electrolyte properties. Small-angle neutron scattering (SANS) is a bulk technique that yields structural information on the one to several-hundred nanometer length scale. Isotopic substitution, most commonly of hydrogen for deuterium, may be employed in SANS to highlight specific structural components. Thus, SANS is well-suited for studying ions in nanopores because the strength of the solvent signal, be it aqueous or organic, may be modulated via isotopic substitution.

In situ electrochemical measurements of a deuterated ionic liquid, and of aqueous electrolytes, in mesoporous and microporous carbon membranes were carried out at different applied potentials over time, as part of the research program of the Fluid Interface Reactions, Structures and Transport (FIRST) Energy Frontier Research Center based at Oak Ridge National Laboratory (USA).[3] For the ionic liquid [C_4mim^+][Tf_2N^-] confined in hierarchical nanometer-scale carbon pores, high number densities obtained from SANS analysis and classical molecular dynamic simulations (cMD) indicate strong RTIL/pore wall interactions mediated by the liquids' intrinsic affinity for the carbon surface and by the surface's rough microporous topology.[1] Neutron spin echo spectroscopy and cMD generally show a slowing of the long-decay time nanosecond-scale collective dynamics; this behavior is ascribed to an effectively immobilized fraction of RTIL at the mesopore wall.[2] The RTIL-micropore interactions are strong enough to perturb the RTIL ions such that some dynamic processes, on the picosecond time scale occur faster within the micropores than in the mesopore confined case. Current progress in developing *in-situ* capabilities for electrochemical measurements at the ISIS neutron and muon facility (UK) (a user facility available to both academic and industry researchers), will also be discussed.

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P-5

THE ELECTROSORPTION PERFORMANCE OF SPRAYED VS PAINTED ELECTRODES

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Over the years, Capacitive Deionization (CDI) has gained increasing popularity as a cost effective desalination technology and as the scientific understanding of the technology is growing, CDI is becoming feasible for feed sources with increasing salt content as evidenced by the increase in electrode electrosorption capacities [1]. Highly effective electrodes show a combination of large specific surface areas and high conductivity, but the number of charged species (capacity) and the rate at which charged species are adsorbed and desorbed (dynamics) are not only a function of what CDI electrodes are made of. In this study, the authors are investigating how capacity and dynamics are influenced by the preparation methods.

The performance of CDI electrodes is expected to change with the porosity of the electrode which is affected by their deposition method, the same way the performance of Fuel Cell catalyst coated membranes (CCMs) is affected by their preparation conditions [2]. A series of electrodes will be produced whereby carbon based electrodes will be painted or sprayed onto ion exchange membranes after which the BET surface area and capacity of the electrodes will be compared.

The authors would like to acknowledge the Water Research Commission of South Africa for their financial support.

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P-6

NOVEL COMPOSITE ELECTRODE FOR THE ELECTROSORPTION OF SPECIFIC IONS IN CDI PROCESS

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Removal and recovery of valuable ions from wastewater has attracted much attention recently. The removal of phosphorous (P) can prevent eutrophication. If phosphorous can be economically recovered at the same time, it will partly overcome the future scarcity of this non-renewable resource. The current phosphorous recovery techniques include chemical precipitation, biological treatment and adsorption method. Nevertheless, these methods have the drawbacks of secondary pollutants, process complexity or low phosphate selectivity and removal rate. To remove ionic substances from salted waters, the capacitive deionization (CDI) has been viewed as an energy-efficient and greener process. However in this process, ions are electrostatically adsorbed on the electrode surface regardless of the types of ions present. Only when the ion-specific electrodes are used, the valuable or toxic ions can be selectively adsorbed for further usage or disposal. Herein, a study on the preparation of phosphate-specific electrodes for CDI applications was first reported.

We fabricated phosphate-specific composite electrodes by modifying a carbon electrode with nanostructured layered double hydroxides (LDHs). The MgMn-type LDH is capable to exhibit high selectivity for the phosphate ion. The SEM and XRD data indicated that MgMn-LDH was indeed immobilized on the surface of activated carbon (AC) and the dominant characteristic peak of MgMn-LDH was observed (Figure 1 and 2). After preparation of composite electrode, the electroadsorption experiments was performed in the solution containing 10 mg/L Na_2HPO_4, Na_2SO_4 and/or $NaNO_3$ by applying a cell potential of 1 V for 30 min. In the presence of competitive anions, the adsorption amount of phosphate was 3.52 mg/g with ion selectivity (Figure 3). Compared with the suspended LDH adsorbent, our composite electrodes showed 16 times higher adsorption rate. It was suggested that the electric-driving force enhanced the specific phosphorous adsorption rate and effectively shortened the adsorption time. These results demonstrated that an ion-specific composite electrode used in CDI was successfully prepared.

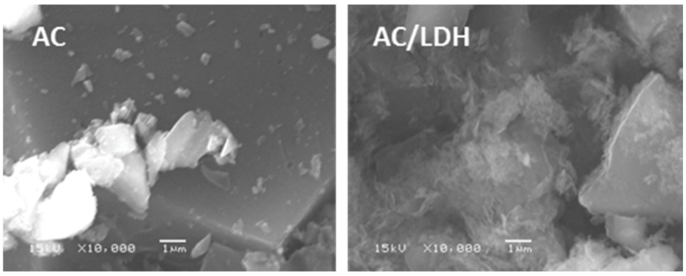

Figure 1. SEM pattern of the activated carbon and layered double hydroxide immobilized on the carbon support.

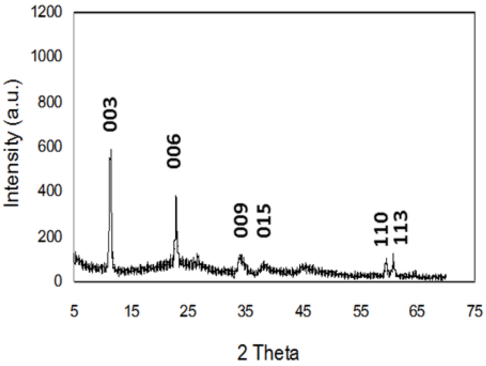

Figure 2. XRD pattern of the AC/LDH composite material.

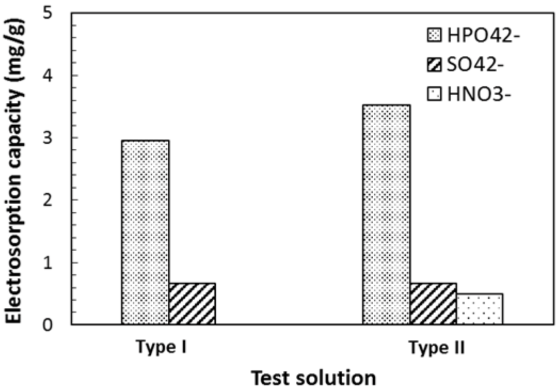

Figure 3. Electrosorption performance of the AC/LDH electrode in the Type I (Na_2HPO_4, Na_2SO_4) and Type II (Na_2HPO_4, Na_2SO_4, $NaNO_3$) solutions.

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P-7

THE EFFECT OF ULTRATHIN METAL OXIDE COATED CARBON MATERIAL FOR ELECTROSORPTION AND CORROSION RESISTANCE IN CAPACITIVE DEIONIZATION (CDI)

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Currently, capacitive deionization (CDI) has attracted attention as low energy consumption and environmental friendly desalination technique, because it can be conducted at low voltages without secondary waste. Especially, carbon materials were used as CDI electrode because it has high conductivity and surface area. In this work, we have synthesized carbon with ultrathin metal oxide layer by atomic layer deposition (ALD) technique and applied to CDI electrodes. And the influence of ultrathin metal oxide on the carbon was studied to the CDI performance. It was identified from TEM, XRD, BET and XPS that the carbon was coated successfully by means of ALD method. Also, as a results of cyclic voltammetry and impedance, it was identified that metal oxide coated carbon electrode has more enhanced electric double layer capacitance maintaining less diffusion resistance like as previous carbon materials. Also charge-discharge and ion conductivity profiles showed that the ion removal ratios of metal oxide coated carbon electrode more than that of previous carbon electrode. Especially, we also analyzed the current density in the localized area. In conclusion, carbon electrodes which was coated by ultrathin metal oxide with high dielectric and hydrophilic properties maintaining its high surface area shows potential for CDI electrode material more effective than previous carbon electrode in CDI system.

P-8

THE SYNERGISTIC EFFECT OF SILVER METAL AND HIERARCHICALLY ORDERED MESOPOROUS CARBONS ON HIGH PERFORMANCE CAPACITIVE DEIONIZATION

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The supply of sufficient clean water for daily demand has recently received consideration attention because of the need of industrial and agricultural activities. Capacitive deionization (CDI) has been regarded as an energy-efficient process to remove a wide variety of ions because of the low energy consumption, low pressure demand and environmental friendliness. Hierarchically ordered mesoporous carbons (HOMCs) has regarded as the promising electrode materials for CDI because of the high specific surface areas and unique pore textures. Although the electrosorption efficiency of HOMCs is better than activated carbons, the electrosorption capacitive of Na ions by HOMC-based materials is usually in the range 39-106 μmol/g. It is known that chloride ions can be easily removed by precipitation in the presence of silvers ion, which may enhance the electrosorption efficiency of ions in solutions. However, the combination of CDI and chemical reaction of silver ions with chloride ions has received less attention.

In this study, the combination of CDI and chemical reaction for the removal of ions was investigated by using HOMCs and silver metal as the cathode and anode electrode materials, respectively. The hierarchically ordered mesoporous carbons (HOMCs) by evaporation-induced self-assembly method was fabricated for CDI application. SEM and TEM images show that the HOCMs contain large domains of highly ordered hexagonal arrays of mesopores with 1-D channels. The specific surface area of HOMCs is 487 m^2/g and the average pore diameters, derived from density function theory, is 3.92 nm with the total pore volume of 0.404 cm^3/g. The C1s XPS spectra of HOMC show three different peaks centered at 284.5, 285.1, 285.5, 286.2 and 289.1 eV, which can be assigned as C=C, C-C C-O, C-O and -O-C=O bonds, respectively. The electrochemical performance of HOMCs shows ideal rectangular voltammograms with Faradic reaction at scan rates of 1-10 mV/s and the specific capacitance of activated HOMC is 20 times higher than that of as-prepared HOMC. In addition, the specific electrosorption capacity of HOMC electrode materials for Na+ removal is 105 μmol/g at 1.2 V. The use of zerovalent Ag and HOMC as the anode and cathode electrode materials, respectively, significantly enhances the removal efficiency of Na^+ ions in solution, and the specific electrosorption capacity of 356 μmol/g is obtained. The excellent electrochemical performance of Ag(0)/HOMC pair is mainly attributed to the increased mesoporous structure and the release of Ag^+ ions to react with chloride ions. In addition, the produced $AgCl_{(s)}$ is precipitated in solutions, which has little influence on the microstructures of HOMC nanomaterials after CDI processes. Results obtained in this study clearly indicate that the combination of Ag(0) and HOMCs is a promising strategy for CDI which could facilitate good charge propagation and fast ion adsorption to treat grey and brown waters.

P-9

ELECTROSORPTION APPLIED TO REMOVAL OF CR (VI) USING ACTIVATED CARBON

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In the tanning and mining industry, the presence of trivalent and hexavalent chromium is often found. Trivalent chromium is known as nontoxic specie, but hexavalent chromium has been cataloged as toxic. Typical treatment to this kind of effluents is chemical precipitation, but it is non-effective when the solutions are diluted (below of 100 ppm). In this way, some technologies have been investigated in order to remove, particularly, hexavalent chromium. In this work, capacitive deionization was studied to remove Cr (VI). Adsorption and electrosorption were carried out to try finding the possibilities that this technology offers to treat this type of effluents. During the adsorption of hexavalent chromium, was found a reduction process, which was influenced by the quantity of mass utilized in this treatment. This information helps to find the best conditioning for the carbon, which is different for anion or cation adsorption. In this way, the electrosorption was designed to catch Cr (VI) in the anode, meanwhile, the Cr (III) formed during the adsorption in the anode, was cached in the cathode. The adsorption for Cr (III) was found as efficient, removing above of 99.5% of the chromium into solution in this form, meanwhile the adsorption of Cr(VI) only represent the reduction stage before to adsorption process as Cr(III).

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P-10

REMOVAL OF ARSENIC FROM GROUNDWATER BY CAPACITIVE DEIONIZATION TECHNOLOGY

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Acute and chronic arsenic exposure via drinking water has been reported in many countries. Various health effects particularly skin diseases and skin cancer can be induced if humans are exposed to arsenic toxicity for a certain period of time. Several technologies including coagulation, adsorption, ion exchange, chemical oxidation, and membrane separation have been used for arsenic removal from groundwater. Arsenic usually presents in natural water at the level of several hundred ppb, associated with the inherent difficulties in developing remediation techniques. Capacitive deionization (CDI) technology has been regard as an innovative process to remove ionic species from aqueous solutions due to low energy consumption and environmental friendliness. Most recently, CDI technology has been proposed for the removal of arsenate (As^{V}) from natural water. However, removal mechanism of arsenic from groundwater with CDI technology is still not well-understood.

In the present study, the feasibility of using CDI technology in the remediation of arsenic contamination of groundwater was evaluated. More specifically, a comparative evaluation for the removal of arsenite (As^{III}) and arsenate (As^{V}) was performed in laboratory-scale CDI experiments using activated carbon electrodes. With further attention to the removal of As^{III} in water, the potential of coupled oxidation and electrosorption of As^{III} under electrochemical assistance was also studied. The experimental results indicated that the removal of As^{III} and As^{V} from water can be achieved by using the activated carbon electrodes at 1.2 V. As^{V} ions were separated by electrostatic interaction, and thus electroadsorbed onto the charged electrode surface. In contrast, As^{III} may be oxidized to be As^{V} ions and electroadsorbed onto the electrode surface simultaneously. Additionally, it was suggested that the presence of sodium chloride or natural organic matter leaded to a decrease in adsorption capacity of arsenic. In a conclusion, CDI shows a great potential for the remediation of groundwater contamination with arsenic at trace concentrations.

P-11

STUDY ON WO_3 GRAFTED CARBON CLOTH FOR CAPACITIVE DESALINATION APPLICATION

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According to recent reports in the literature the combination of metal oxide with carbon materials has great potential to improve the specific capacitance and thus the efficiency of capacitance deionization (CDI) systems. To date TiO_2, ZnO and MnO_2 are the most frequently investigated metal oxides for CDI applications.[1-5] However, although the involvement of these metal oxides improves the electrosorption capacity, these have poor stabilities when exposed to acidic or basic solutions. Compared with these metal oxides, tungsten oxide exhibits better stability and WO_3 is the most preferable candidate as the cation storage containers in the electrochromic applications.[6-7] Nevertheless, there is a lack of reports on WO_3/carbon-based materials for CDI applications. Hence, in this work carbon cloth (CC) grafted with tungsten oxide was employed as cathode for CDI applications, which was successfully synthesized by a hydrothermal method.

The oxide was mainly composed of flaky WO_3, and uniformly distributed over the surfaces of CC. These as-synthesized WO_3 flakes are vertically adhered on the whole carbon cloth as shown in Fig. (a). Accordingly, the atomic ratio of W/O is 3:1 confirmed through the SEM-EDS and BET revealed that the specific surface area of WO_3 deposited carbon cloth is approximate 25 $m^2.g^{-1}$, 31.25 times of 0.8 $m^2. g^{-1}$ of the bare carbon cloth 0.8 $m^2. g^{-1}$(Fig 1(b)). This enhancement is a promising advantages for the ion adsorption needed in CDI applications.

The preliminary desalination experiments were conducted in the static 0.01M NaCl aqueous solution at a scanning rate of 100mV/s over a potential range from -1 V to 1V vs SCE (Fig 1(c)). As the result of the increased surface area, the modified carbon cloth attained an enhanced salt removal efficiency, i.e., about 40 times larger than the bare carbon cloth. Based on present estimation, after 90 seconds, the NaCl can be reduced 1.17% from 0.01 M NaCl solution (Fig 1 (d)). Further experiments and adaptations to the metal oxide/carbon electrodes are ongoing the results of which will be shown in the presentation.

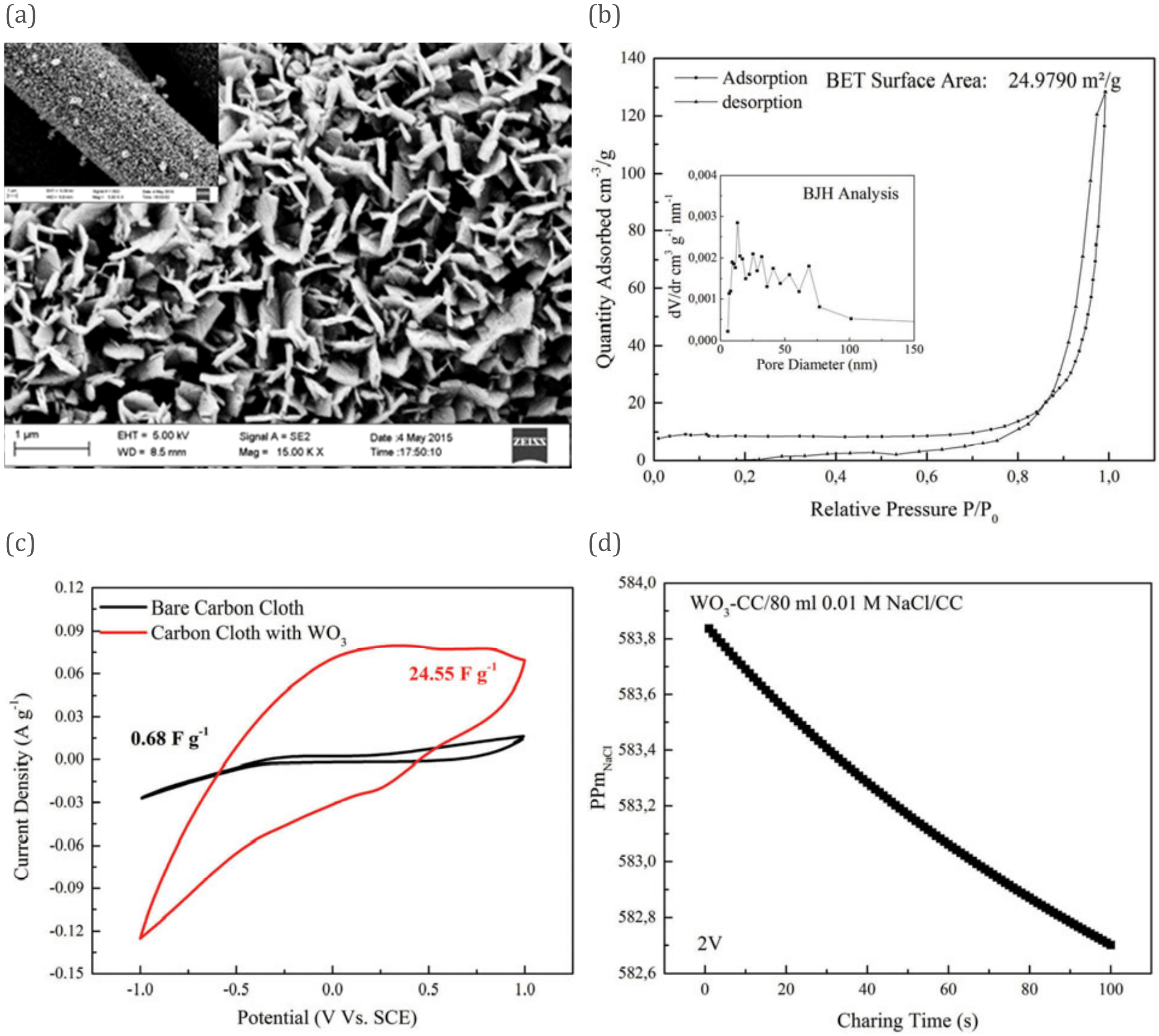

Figure 1

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P-12

PUTTING THE ELECTRIC DOUBLE LAYER TO WORK IN VARIABLE CAPACITANCE ENGINES

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Variable capacitance engines operate by charging and discharging electrodes at alternating high and low capacitance, respectively. Crucial to the working of these engines is the electric double layer which forms near the surface of the charged electrodes. This layer of counter-ionic charge can be modeled at various levels of sophistication, most notably by Poisson-Boltzmann theory (PB) and extensions thereof [1]. One finds that the capacitance has dependence a set of parameters which can be tuned independently to achieve variable capacitance.

A lot of work in recent years has focused on electrolyte-filled nanoporous supercapacitors where variable capacitance of the electric double layer is achieved by changing the properties of the *electrolyte.* An example well known to this community is CAPMIX, which exploits variations in electrolyte concentration [2]. Further options include variations in temperature in capacitive thermal energy extraction [3], or even combinations of thermal and concentration steps simultaneously [4].

On this poster I furthermore present recent work on a capacitive engine whose variable capacitance is caused by a change in *geometry*, brought about by a mechanical stimulus [5-7]. The engine consists of two parallel capacitor plates bridged by liquid droplets, which are periodically squeezed by adjusting the plate separation. A change in configuration changes the capacitance, driving a current in the external circuit. This system could for instance be used to harvest mechanical energy from ambient vibrations. As such it could provide a valuable alternative to batteries in portable electronic devices which require only small amounts of electric power.

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P-13

CAPACITIVE DEIONIZATION PROCESS USING PILOT SCALE MODULE OF CARBON ELECTRODES COATED WITH ION EXCHANGE POLYMERS

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Capacitive deionization (CDI) has the potential to be an energy efficient desalination process [1, 2]. To be competitive for brackish water applications, cost effective industrial scale manufacturing and operation are needed.

CDI testing for water desalination was carried out through the pilot scale module of carbon electrodes coated with ion exchange polymers. Sulfonated polystyrene and aminated copolymer were prepared as a cation exchange polymer and an anion exchange polymer, respectively. The ion exchange polymers were coated onto the surface of carbon electrodes as an ion-selective layer via a roll to roll coater (Fig. 1).

The coating layers of 10∼20㎛thick were formed much thinner than commercial ion exchange membranes of about 150 ㎛ used in membrane capacitive deionization (MCDI) in general. The performance of the pilot scale module equipped with 50 pair electrodes coated with the above mentioned polymers was investigated in terms of salt removal efficiency and energy consumption in different CDI operating conditions as illustrated in Fig. 2. For effluent salt concentration, comparison between CDI using our coated electrodes and MCDI comprised of commercially available ion exchange membranes was made as a function of adsorption time in the ion removal step. Due to thin ion-selective polymer layers, CDI process using our electrodes coated with the polymers could be cost effective for module design and manufacturing as compared to MCDI with commercial ion exchange membranes.

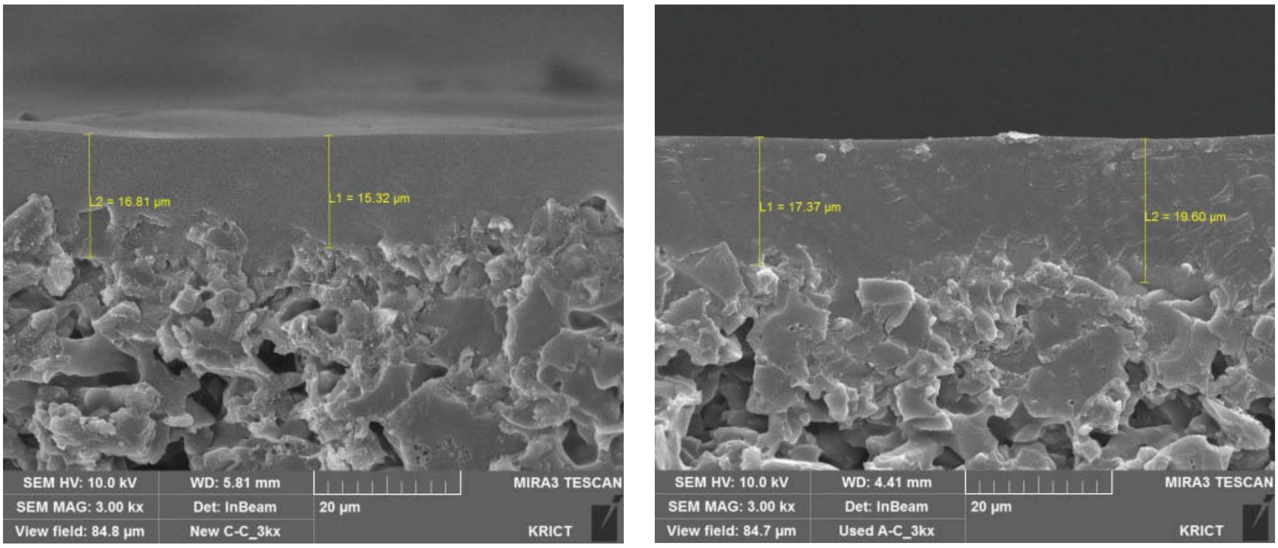

Fig. 1. SEM images showing the cross section of sulfonated polystyrene coated electrode (left) and aminated copolymer coated electrode (right).

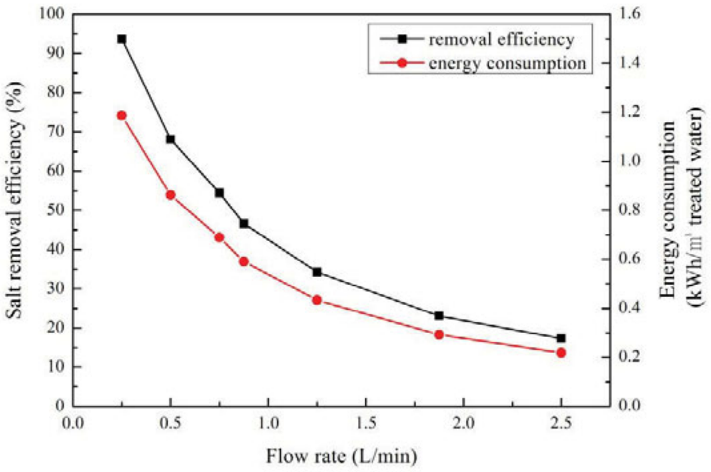

Fig. 2. Salt removal efficiency and energy consumption as a function of feed flow rate. Feed water slat concentration: 1850 mg/L

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P-14

EFFECT OF THERMAL TREATMENT ON SUGAR CANE BAGASSE FLY ASH ELECTRODES FOR CAPACITIVE DEIONIZATION

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Water scarcity represents a critical issue in many areas of the planet. In addition, severe droughts experienced in regions unaccustomed to face these kinds of difficulties have increased concern about the importance of this resource. That is particularly true of Brazil, which has the 8% of the fresh water reserves in the planet. Nevertheless, the unequal distribution of water resources in the Brazilian territory (3.3% in the northeast semiarid region where 27% of the population lives while 80% of these resources are in the much less populated Amazonian area) along with recent drought experienced by regions like the city of São Paulo have raised a discussion about water resources management. Besides the reduction of the demand, which could be achieved by using more cost effective and low energy consumption technologies, a feasible solution for the Brazilian semiarid region could be oriented to increase the water resources available by implementing brackish groundwater desalination technologies.

Of all the different technologies currently employed for brackish water desalination, an emerging technology, the capacitive deionization (CDI), has attracted the attention of the scientific community over the last decade. CDI works by applying a voltage between a pair of electrodes immersed in a solution, forcing the ions, in this fashion, to be retained in the electrochemical double layer formed at the interface between the porous electrodes and the treated solution. Once the electrodes become saturated, a short circuit or a potential inversion is conducted in order to prepare the electrodes for the next removal cycle. This mechanism, that presents certain similarities with the supercapacitor technology, has also the potential to retrieve part of the energy employed, making the process in this way, even more energy efficient.

One of the most important requirements in order to make CDI competitive with current technologies (such as reverse osmosis or electrodyalisis) is the cost of the electrode materials. Hence, an important cost reduction could be achieved by using biomass-waste carbonaceous materials as CDI electrodes. Following this idea, in this work, electrodes fabricated from fly-ashes obtained from the ethanol-sugar Brazilian industry were analyzed as a potential material for CDI. In addition, the effect of the heating temperature during pyrolysis (between 200-800 °C) on the structural and electrochemical properties of the electrodes was evaluated. Thus, physical (surface resistivity, wettability, specific surface area, and pore size distribution) and electrochemical (specific capacitance) characterizations were studied. Moreover, desalination experiments were performed in order to measure electrosorption capacity and the ion removal kinetics.

The results obtained in this work showed that a significant improvement in terms of specific capacitance was achieved by pyrolyzing the sugar cane bagasse fly ashes (SCBFA) at 200 °C (named T200) before mixing them with the binder and organic solvent in the electrode preparation process (Fig. 1). Additionally, batch electrosorption experiments were conducted at 1.2 V using a 600 ppm NaCl solution. The results were in accordance with the capacitance trends displayed in Fig. 1 showing that the highest ion electroadsorption values were obtained for the T200 electrodes. Moreover, not only was the electrosorption capacity for ions increased but also ion removal kinetics were substantially improved when SCBFA were pyrolyzed at 200 °C. The authors believe that the better wettability of these T200 electrodes over the rest of the materials tested has a critical impact on the degree of electrosorption.

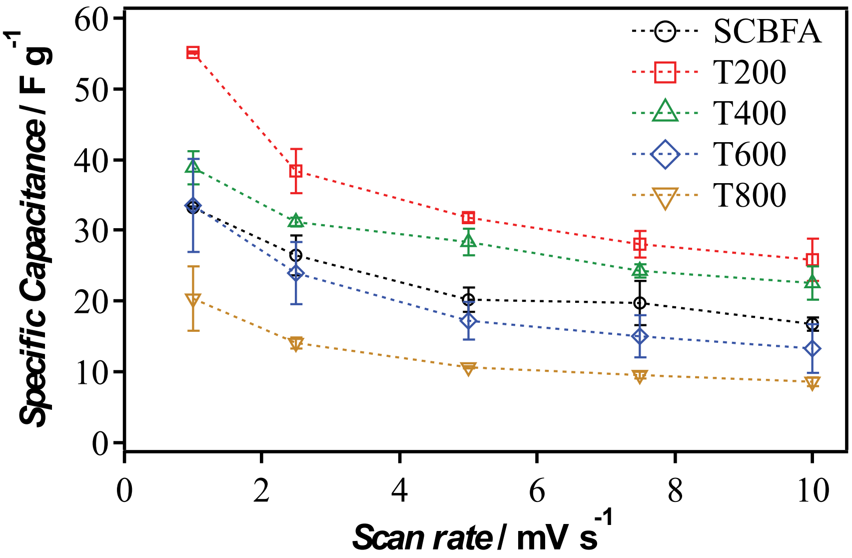

Figure 1. Effect of the temperature employed during the pyrolysis process on the electrode specific capacitance as a function of the scan rate.

P-15

ANALYSIS OF PARAMETERS AND OPERATIONAL CONDITIONS OF LOW-COST ELECTRODES FOR CAPACITIVE DEIONIZATION

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The scarcity of water resources has been stimulating the development of more energy efficient technologies for providing fresh water. In this scope, water desalination may play an important role due to the significant amount of available resources (brackish and sea water) in the planet. In the past few years, capacitive deionization (CDI) has been emerging as a low-cost water desalination technology especially recommended for low-medium concentration streams (2000-5000 ppm). In the CDI field, one of the most investigated topics has been the study of different carbon materials as CDI electrodes. Among the different factors affecting the feasibility of the CDI technology, the cost of the electrodes seems to be a critical issue. Based on this idea, inexpensive carbon materials, commercially available, were evaluated in this study as electrodes for CDI. A preliminary study based on a physical and electrochemical characterization of these materials, determined that the activated carbon (AC) demonstrated superior performance compared to other carbon fabrics.

Henceforth, a factorial design of experiments was prepared to analyze the influence of the cell potential (E_{cell}), mass of AC (m_{AC}), addition of carbon black (%CB) and electrode voidage on the ion removal capacity, charge efficiency and specific energy consumption. CB was added to the AC electrode in order to enhance its conductivity and the addition of NaCl was used as an attempt to create interparticle macropores for the purpose of improving electrode permeability. The results demonstrated that neither CB nor NaCl had a single effect over the electrode performance. On the other hand, according to Fig. 1, an interaction between electrode thickness and electrode voidage (expressed in terms of %NaCl) was found to be beneficial in terms of salt removal capacity for the thickest electrode.

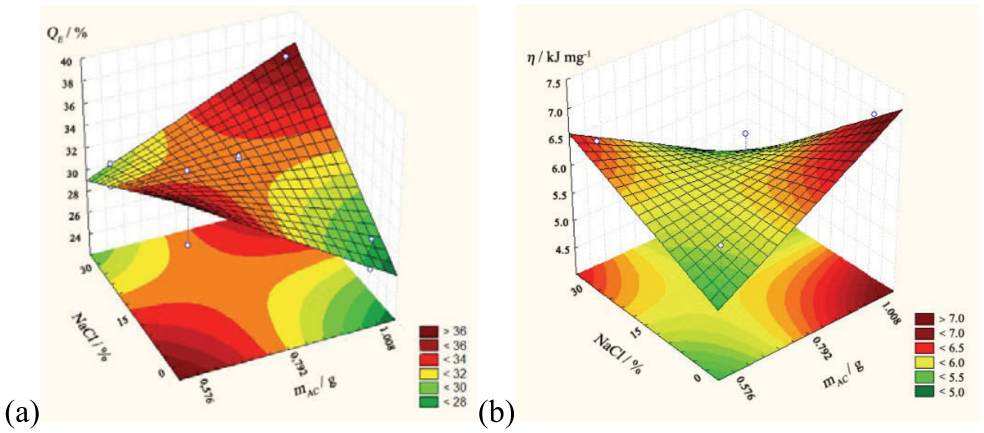
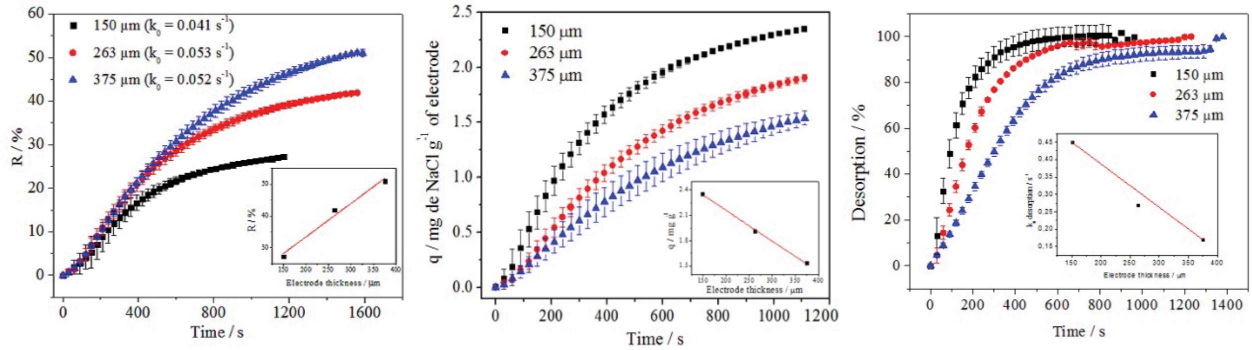


Fig. 1 - Response surfaces for *charge efficiency* (a) and *specific energy consumption* (b) as a function of m_{AC} and *%NaCl*. *%CB* = 4.5 and E_{cell} = 1.2 V.

A detailed investigation of the influence of m_{AC} regarding to the effect of electrode thickness was carried out in order to understand their influence on the CDI performance. The results demonstrated that the increase on the electrode thickness was not proportional to the amount of ions removed. This finding suggested that part of the active material was not efficiently used on the ion electrosorption process which could be explained based on the uneven potential distribution on porous materials. Moreover, while the kinetics of electrosorption was found to be independent of the electrode thickness, slow desorption kinetics were detected for thick electrodes (Fig. 2). Thus, the investigation of electrode thickness has shown that must be an optimum point where the ion removal and the kinetics of sorption and desorption could be maximized.



(a) (b) (c)

Fig. 2. *R* (a) , *q* (b), and desorption against time (c) for the AC electrode with different thicknesses. E_{cell} = 1.2 V; C_0 = 300 mg L^{-1}.

P-16

IMPROVEMENT OF CHARGE EFFICIENCY BY ASYMMETRIC CAPACITIVE DEIONIZATION

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Desalination is currently a very topical area of research for water purification. Capacitive deionization (CDI), as a new desalination technology, is developing very fast in recent year by exploring new electrode materials, designing CDI reactor structure and optimizing the operation parameters[1], because of its merits such as low energy consumption, high water recovery rate, the renewability of the electrode and easy operation with no secondary pollution due to low applied voltage [2, 3]. Charge efficiency (CE), defined as the ratio of the equivalent charge of adsorbed salt to the total charge input during charging process, is one of the most important parameters in CDI cell. CE can be increased by membrane-based CDI cell[4] or by chemical modification of the electrode surface [5, 6] to diminish co-ions migration/repulsion. Activated carbon (AC), as the most commonly used commercially available and cost efficient carbon material, is still attractive as the typical CDI electrode material because of its high specific surface area, low cost, easy manufacturing on a large scale [2, 7].

In this presentation, several asymmetric activated carbon composite electrode capacitors such as amphoteric metal oxides ZnO-AC‖AC, sulfonated graphene(GP-SO3H)-AC‖AC, aminated graphene (GP-NH2)-AC‖AC, will be reported in order to well understand the effect of the surface Zeta potential of the composite electrode materials on charge efficiency of CDI. The sulfonated graphene(GP-SO3H)-AC‖AC capacitor had the highest CE value of 90%, much higher than AC‖AC symmetric capacitor (40%). The relationship of CE with zeta potential was obtained. It demonstrates that the non-membrane chemical modification on the carbon electrode materials is feasible to arrive at the high charge efficiency. With zinc oxide/activated carbon composite electrode (ZnO/AC) as a candidate, the mechanism was analysed based on pH variation of electrode surface and the zeta potential of ZnO. This research provides a particularly important base and guidance for the selection of electrode materials in capacitive desalination in order to realize the long term stability.

Acknowledgments:

This work was financially supported by the National Natural Science Foundation (No. 21105009, 21476047), the Fundamental Research Funds for the Central Universities (2232012A3-05,) and foundation of State Key Laboratory of Electroanalytical Chemistry (SKLEAC201205).

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P-17

ELECTROCHEMICAL CHARACTERISTICS AND ELECTROSORPTION PERFORMANCE OF ACTIVATED CARBON ELECTRODES IN CAPACITIVE DEIONIZATION

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Due to climate change and unsustainable withdraw of water resource, water scarcity has become one of the most urgent problems in the world. In recent years, capacitive deionization (CDI) technology has been considered a promising alternative desalination process due to its energy efficiency, easy operation, environmental friendless. CDI process follows the same working principle of charge separation with electrical double-layer capacitor. However, electrochemical characterization of nanoporous carbon electrodes is associated with the inherent difficulties to determine the desalination performance at low salt concentrations.

The objective of this study is to provide electrochemical fundamental and practical aspects of electrosorption performance of activated carbon electrodes in CDI process. Electrochemical characteristics in terms of capacitance and electrical resistance were measured by cyclic voltammetry (CV), and galvanostatic charge-discharge (GC) and electrochemical impedance spectroscopy (EIS) tests with salt concentrations ranging from 2 mM − 1 M. Single-pass flow CDI system was carried out to investigate the desalination performance of activated carbon electrodes at different slat concentrations 2−50 mM. The effective surface area of electrodes was 20 cm × 30 cm and the applied voltage was 1.0 V. As a result, the double-layer capacitive behaviours are very different at 1 mM, 10 mM, 0.1 M, and 1 M NaCl. Activated carbon electrodes operated at relatively lower NaCl concentration had lower specific capacitance, larger iR drop, and higher electric resistance, reflecting the restriction of ion transport from bulk solution onto the electrode surface. It implies that the desalination performance of activated carbon electrodes strongly depends on the initial salt concentration. As evidenced by the CDI tests, increasing NaCl concentration from 2 mM to 50 mM, the electrosorption capacity increased from 3.8 mg/g to 6.0 mg/g, respectively, suggesting the improved ion-accessible surface area and less electrical double-layer overlapping effect. One can see that the desalination performance is much related to the capacitive characteristics at relatively low salt concentrations (2−50 mM). Also, the charge efficiency increased with increasing the NaCl concentration. Therefore, charge capacity and charge efficiency are key factors to determine the desalination performance in CDI.

P-18

DEVELOPMENT OF SPIRAL ELECTRODES FOR CAPACITIVE WATER DEIONIZATION

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Capacitive deionization (CDI) is a promising technology for water treatment with low level of salts concentration. Typical application of CDI is desalination of brackish water and selective removing unwanted ions like nitrates and nitrites. Currently the most used desalination processes are electrodialysis (ED), reverse osmosis (RO) and ionex-beads (IB). These technologies are typical large scale applications with high investment costs. CDI has many advantages in comparison with mentioned technologies. CDI is more energy-efficient and typical units have compact design. Units can be designed from small capacity, typical ten of litres per hours, to large with capacity thousand litres per hour. Investment cost of this units is lower than units for ED and RO. CDI does not need regeneration solutions like IB, because waste is only water with elevated concentration of ions, which was on feed into unit.

High surface carbon, typical more than 1000 $m^2 g^{-1}$, is necessary to use for porous carbon electrodes for CDI. High surface carbon is typical produced for absorbents and filters in form carbon black. Carbon black have to be mixed with binder for ensure mechanical resistance. Polyvinylidene fluoride (PVDF) is most often used binder of carbon black in carbon porous electrode, these binder is nontoxic, but toxic are its solvents. Tetrahydrofuran, methyl ethyl ketone, dimethylsulfoxide and cyklohexanone are used as solvents for applications of PVDF. These solvents are toxic, irritant or damaging the environment and their residues can be contained in binder. In this work we focused for possibility of polyvinyl acetate application as a binder. It is nontoxic and as solvents can be used ethanol, which is also environmentaly acceptable. This work describe influence of binder content in mixture to final capacity of electrodes. Compare deposition of carbon porous layer to current collector by air-brush and casting method.

One way for increasing unit capacity is applying spiral electrodes. These arrangement allow increasing performance of modules by compact design. Flexible electrodes with flexible current collector are necessary for construction of spiral modules. Aluminium foil is promising material, which can be used as current collector. This work described influence of binder content in mixture to mechanical properties of carbon porous electrodes. Also its flexibility for spiral geometry was evaluated.

Acknowledgments:

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P-19

SIMPLIFIED THEORY FOR SALT ADSORPTION IN CAPACITIVE DEIONIZATION

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The desalination process using capacitive deionization (CDI) is based on the electrostatic adsorption of ionic compounds from water under the influence of an electrical field between pairs of porous electrodes. The cations and anions migrate to oppositely charged electrodes, and absorb inside them. This phenomenon of electrosorption is linked to two processes that occur jointly: i) the transport of ions through the open space between the carbon particles that make up the electrode, which we refer to as macropores, and ii) the transfer of ions from the macropores into the pores inside the carbon particles, these we call micropores. To describe the adsorption process, we present a dynamic theory in which we assume the transport of ions from macropores to micropores to be rate-limiting, compared to the ion transport across the electrode. With this assumption, all relations describing the transient response of the electrode become invariant across the electrode thickness, and the complete response of the CDI cell, regarding to ion concentrations and charge density, is predicted by a “zero-dimensional” model. We developed the theory to represent transient desalination processes considering mono-electrolyte solutions and systems with and without ion-exchange membranes (IEMs) in front of the electrodes.

We compare our theory with experimental data obtained in a wire-CDI cell, consisting of electrodes with a thin porous carbon layer coated onto graphite wires. The theoretical data closely reproduce the actual ion adsorption phenomenon observed in experiments.

P-20

PREPARATION AND CHARACTERIZATION OF ION EXCHANGE MEMBRANE WITH HIGH ION EXCHANGE CAPACITY FOR EAD PROCESS

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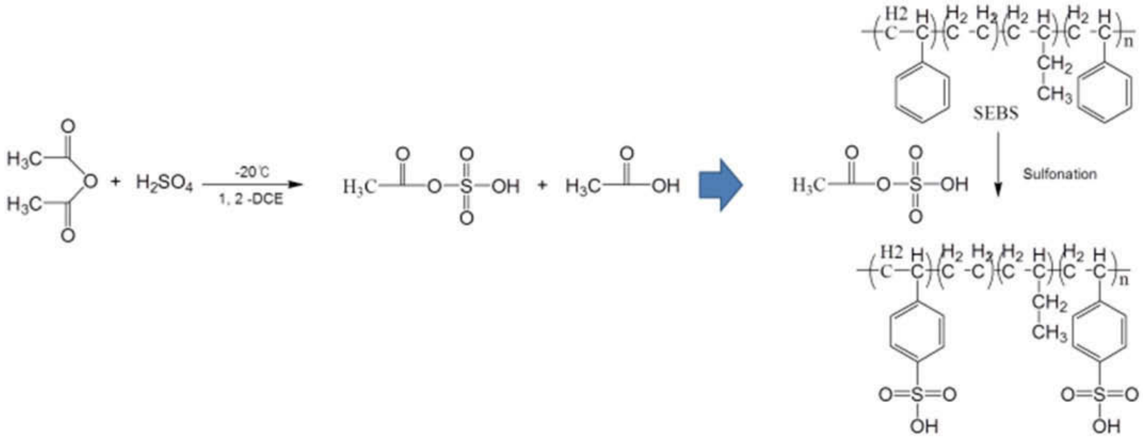
Recently, electro-deionization process is considered to be an energy-efficient technology for brackish water desalination compared with reverse osmosis and distillation. This is mainly because electro-deionization process removes the salt ions from the water, while the other technologies extract the water from the salt solution. Most current capacitive deionization or electro-adsorption systems typically utilize high surface carbon in a variety of forms. Unlike this system, EAD (Electro-adsorptive de-ionization) process is composed of the module with bipolar membrane and the ion exchange resin. Basically, the ion exchange resin is inserted into each membrane to improve their electro chemical property. Therefore, homogenous size distribution and the equivalent ratio of the ion exchange resin are very important factor in determining the performance of the system.

In this study, we prepared the ion exchange membrane based on rubbery polymer such as sulfonated SEBS (styrene-ethylene-butylene-styrene copolymer) and the polymeric nanoparticles with higher ion exchange capacity were added into the SEBS membrane. Finally, the performance of the prepared membrane was measured for EAD application.



Scheme 1. Synthetic route of sulfonated SEBS (styrene-ethylene-butylene-styrene copolymer)

P-21

EFFECT OF CARBONS POROUS TEXTURE ON THE CAPACITIVE DEIONIZATION OF WATER

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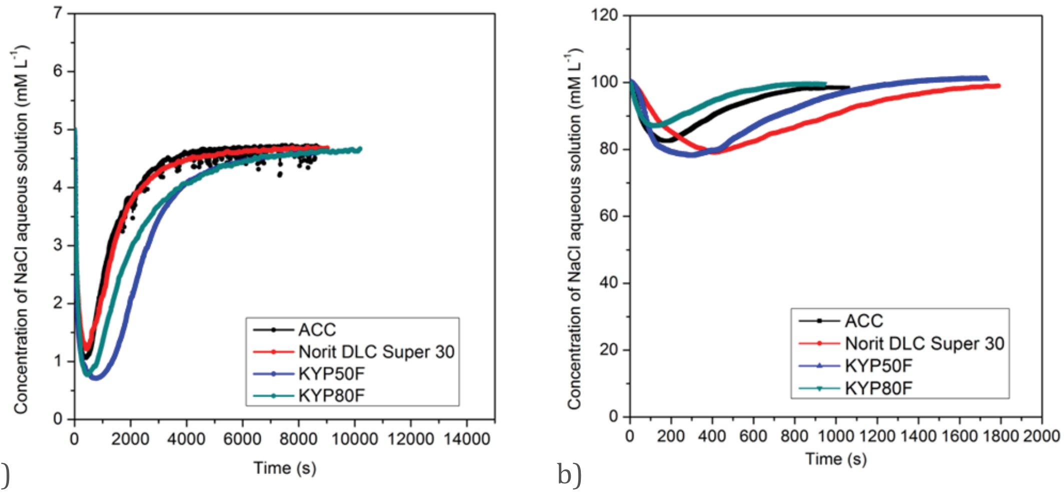
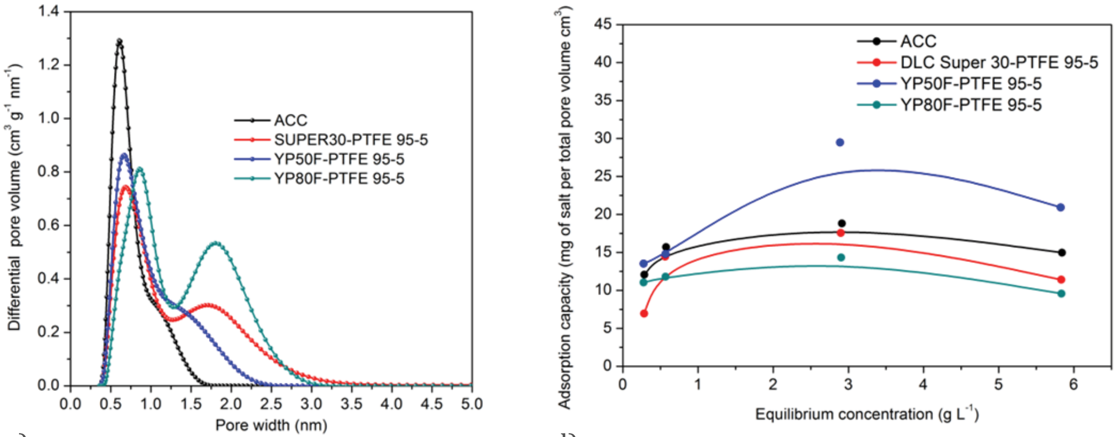
Capacitive deionization (CDI) is based on applying an electrical potential difference between two carbon porous electrodes to reversibly immobilize salt ions inside the pores by electrostatic forces [1,2]. Carbon materials widely used for electrochemical capacitors application can be implemented in CDI techniques successfully [1, 3].

In the present work, activated carbons (AC) with various porous texture characteristics have been used for NaCl removal from water at initial concentrations of 0.005, 0.01, 0.05 and 0.1 mol L^{-1}. Electrodes containing 95% AC and 5% PTFE binder were prepared from the AC powders; a self-standing activated carbon cloth (ACC) was also used to get rid of the binder. The effect of several parameters (initial salt concentration, applied voltage up to 1.2 V, …) on the CDI performance was studied. Figures 1a and 1b show the evolution of NaCl concentration at the outlet of the CDI cell vs time with a flow rate of 1.5 ml L^{-1}, for electrodes made of different activated carbons and an initial NaCl concentration of 0.005 mol L^{-1} and 0.01 mol L^{-1}, respectively. It is visible that, applying a polarization allows to reduce the NaCl concentration in the effluent to a minimal value, after which the concentration returns back to a higher equilibrium value revealing saturation of carbon porosity. In figure 1d which shows for all carbons the plot of adsorbed amount of salt per unit of total pore volume vs the equilibrium concentration, the highest adsorption capacity is observed for the Kuraray YP50F carbon and the lowest for the Kuraray YP80F. Taking into account the pore size distribution data (Figure 1c), it seems that essentially microporous materials, with pore diameter smaller than 2 nm, are more suitable for the adsorption of ions than those containing a relatively noticeable amount of mesopores. Hence, capacitive deionization is a suitable and reversible technique for the desalination of water containing low concentrations of salt (below 100 mmol L^{-1}).



a) b)



c) d)

Figure 1: NaCl concentration vs time for different electrodes materials after CDI of (a) 0.005 mol L^{-1} NaCl solution at 1.2V and (b) 0.1 mol L^{-1} NaCl solution at 1.2V; (c) pore size distribution of carbons by the 2D-NLDFT method; (d) adsorption capacity vs equilibrium concentration for various electrode materials.

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P-22

FEASIBILITY STUDY ON CAPACITIVE DEIONIZATION PROCESS FOR HIGHLY CONCENTRATED IONS OF WASTEWATER

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CDI system can be organized for remove target ions depending on the ionic strength.

This study was performed to evaluate the feasibility of CDI technology for removal of highly concentrated NH_4-N and PO_4-P in wastewater.

The CDI module consisted of 100 pairs of electrodes. The influent water is wastewater with its highly concentrated NH_4-N (1,570mg/L) and PO_4-P (244mg/L). The operating potential was D.C. 1.5 V. In experiment method, batch type of charging 1 minute and discharging as 1.5 minutes proceeded after inflow of wastewater into CDI module. Charging and discharging as 1 cycle, 40 cycles proceeded.

As the results, the removal efficiencies of NH_4-N and specific adsorption was 76%(40 cycle), 0.96 mg/Cell-Cycle. The removal efficiencies of PO_4-P was 76% (40 cycle), specific adsorption was 0.11 mg/Cell-Cycle. As shown in Fig. 1., the graph was divided into 2 phases.

First phase; the accumulative adsorption amount was increased with linearly. Second phase was saturated with ions, so it was not absorbed anymore.

In the case of NH_4-N, the removal efficiencies was 60% during 10 cycles, it was similar to removal efficiencies of 40 cycles. PO_4-P, also, was removed 65% during 14 cycles.

These results can be used as a determining the operation conditions to remove ions. And CDI was evaluated to be suitable for removing of ions from wastewater.

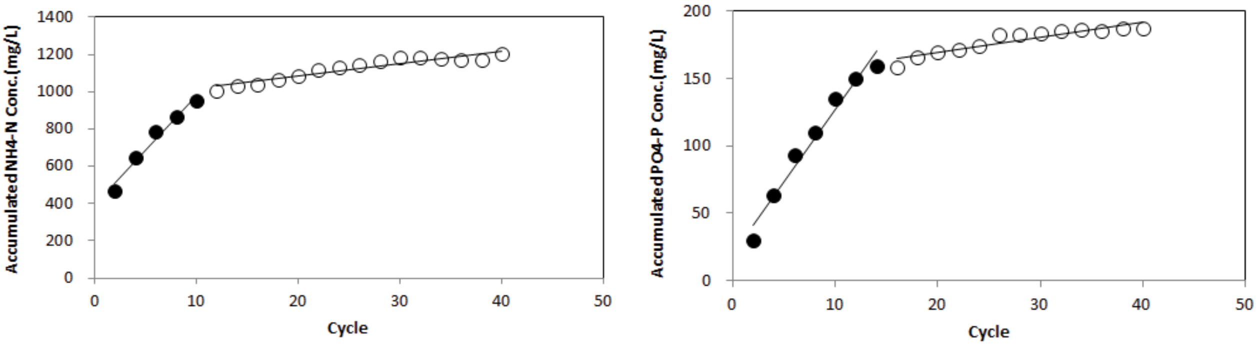

Fig. 1. The graphs of accumulated adsorption ions

P-23

MICROBIAL CAPACITIVE DESALINATION FOR ORGANIC AND SALT REMOVAL

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This study presents an integrated technology called microbial capacitive desalination (MCD), which takes advantage of the synergy between microbial electrochemistry and capacitive deionization to remove both organic contaminants and salts in one reactor and at the same time producing electrical energy. Since our first publication in Energy & Environmental Science in 2012, we have scaled the systems from lab scale to pilot scale, and a variety of wastewater and saline water streams have been tested. This study summarizes the principle of MCD and its relationship with CDI, as well as experimental results associated with the technology.

Figure 1 shows the schematic of a microbial capacitive desalination (MCD) for simultaneous organic and salt removal and energy production. Contaminated water can be fed into all 3 chambers. When microorganisms in the anode chamber oxidize organic substrates during anaerobic respiration, they deliver electrons to the anode electrode. The electrons (i.e. current) flow through an external circuit to capacitive membrane assemblies in the middle chamber, and finally combined with protons in the cathode chamber to generate water. Charged ions are adsorbed on to the membrane assembly due to potential generated across the electrodes. Electrical energy can be generated during capacitive discharge of the middle chamber. We tested system performance in both lab and pilot scale reactors using real wastewater samples collected in Colorado.

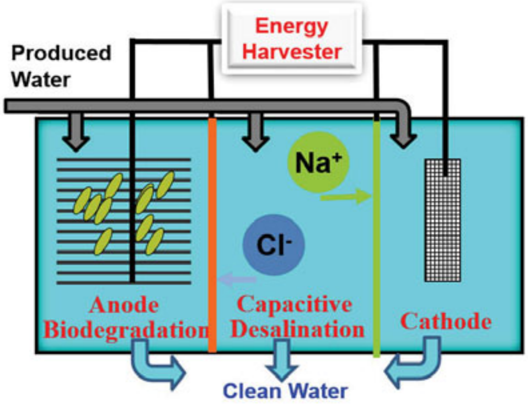

Figure 1: Schematic of MCD principle. Contaminated water flows into all 3 chambers, and after microbial and electrochemical treatment, water and energy are collected for reuse.

For lab scale 5 gallon per minute lab scale reactor, it was able to remove total dissolved solids (TDS) at the rate of 2,760 mg TDS/L/hr and chemical oxygen demand (COD) at a combined rate of 170 mg COD/L/hr, respectively5. The MCD had a Coulombic efficiency of 21.3%, and during capacitive deionization regeneration, 1789 mJ/g activated carbon cloth (ACC) was harvested. One advantage of MCD is that all three chambers could be used to remove both organic and inorganic contaminants. The reactor removed greater than 65% of the TDS and 85% of the COD in 4 hours of operation in the desalination chamber, and more than 98% of the salts and 75% of the organics were recovered during regeneration process. The activated carbon adsorption level was 65.6-68.2 mg TDS/g ACC, and greater than 98% of the adsorbed ions can be recovered during regeneration for the first 2 cycles. For the pilot scale system consists of multiple MCDs, a peristaltic pump, an energy harvesting system, 7 sensors, data collection and an automation control system. The pilot system is operated at flow rate of 0.6L/min (228 gallons/day), and is capable of removing 0.3 mg COD/L/min (473 mg COD/L/Day) from the anode chamber and 0.5 mg COD/L/min (724 mg COD/L/day) from the desalination chamber. From the desalination chamber 66% of the TDS was removed at a 50% water recovery rate. The highest power density achieved from a single MCD was 89 W/m3 with a coulombic efficiency of 11.4% (Figure 2).

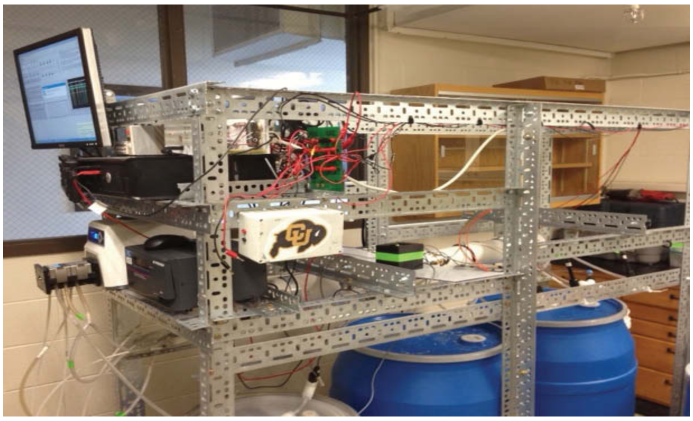

Figure 2. An image of the pilot MCD system.

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P-24

POROUS ELECTROACTIVE POLYMER HYBRID FOR ELECTROCHEMICALLY CONTROLLED SEPARATION OF METAL IONS

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Water pollution by heavy metal ions can pose serious environmental and health concerns. Various treatment methods to remove heavy metal ions involve adsorption, chemical treatment and membrane separation. Adsorption using activated carbon, zeolite or silicone is common due to its feasibility and low cost. However, the regeneration of the adsorbent relies on chemical changes in solution conditions. Capacitive deionization, on the other hand, relies on the electrosorption in the electric double layers to remove salt ions and requires only electrical potential swings, not addition of other chemicals, for the release of adsorbed species. Means for enhancing selectivity are an active area of research.

Here we developed an electrochemically controlled selective separation method for metal ions via chelation and charge repulsion. An electroactive polymer hybrid-coated conductive carbon substrate was used to reversibly adsorb and desorb metal ions from aqueous solutions by varying the applied electrochemical stimuli. The polymer hybrid was fabricated by simultaneously electro-polymerizing polypyrrole and electro-precipitating polyvinylferrocene. The formed hybrid exhibited a highly porous morphology with a high specific surface area of ~ 160 m^2/g. When reduced, the amine groups of polypyrrole chelated with metal ions. The high surface area of the polymer hybrid facilitated the access of metal ion to the polymer hybrid, thus increasing the adsorption capacity of the polymer. Upon the application of a positive potential, the oxidation of the polypyrrole resulted in a reduced chelating effect and the introduced positive charges led to the release of metal ions by charge repulsion. The concentration of copper ions was monitored *in situ* by cyclic voltammetry and quartz crystal microbalance. The surface morphology of the polymer coated composite before and after adsorption was studied via scanning electron microscopy. This novel method allowed selective reversible adsorption and desorption of metal ions from aqueous media via simple electrochemical control.

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THE EXCELLENT WATER SOFTENING EFFICIENCY USING ACTIVATED WASTE COFFEE GROUND ELECTRODE IN CAPACITIVE DEIONIZATION

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In this work, we introduced the activated waste coffee grounds (WCG), a high effective electrode material which was first time used for capacitive deionization (CDI) process. WCG was activated to significantly improve surface area, electrochemical activity and electric conductivity by the simple thermal treatment. Along with other advantages such as available, cheap and environmental friendly properties, WCG can be considered a promising electrode material for CDI units. The hardness removal capacity of electrodes reached 4.4 mg g^{-1} at applied voltage of 1.5 V which is better than almost conventional activated carbon materials in water softening technology.

Keywords: Capacitive Deionization, Waste Coffee Grounds, Activated Waste Coffee Grounds

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