May 26-28, Leeuwarden

IAP 2014 Interfaces in Water and Environmental Science

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centre of **excellence** for
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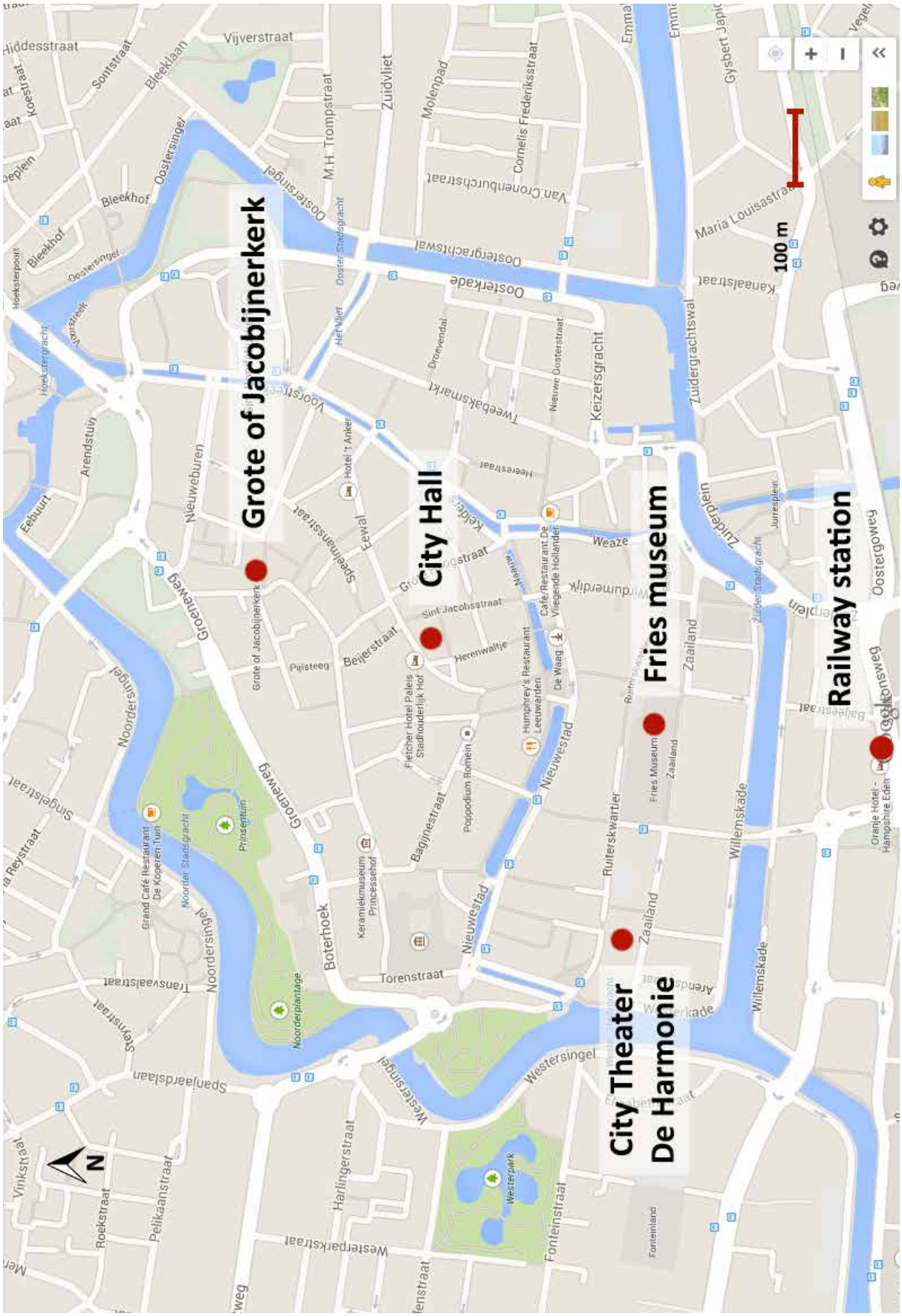

Leeuwarden, City Center

Welcome

The 8th International Conference Interfaces Against Pollution (IAP2014), held in Leeuwarden, the Netherlands from May 25 to 28, is part of a proud series of conferences initiated in Wageningen (The Netherlands, 1997) and followed in Miskolc (Hungary, 2002), Julich (Germany, 2004), Granada (Spain, 2006), Kyoto (Japan, 2008) , Beijing (China, 2010) and most recently in Nancy.

IAP conferences seek to provide a forum for researchers working in the interdisciplinary field of Environmental Science. Colloids and lnterfaces in natural and engineered media are at the heart of the conference. This includes topics of societal concerns like environmental protection, remediation of polluted sites, water treatment, optimization of mineral resources and the impact of nanotechnology residues on the environment.

IAP has a broad, but fundamentally scientific scope, which has broadened over the years. The IAP 2014 specifically has shown to attract a large community in the field of capacitive desalination. In line with the wide spectrum of disciplines (physics, biology, physical chemistry, mineralogy) relevant for environmental science, IAP2014 is intended to cover research from work at the nano-, meso- and macroscopic scales, from transient processes to equilibrium.

The international IAP advisory council and the local IAP2014 organization committee would like to thank our sponsors Gemeente Leeuwarden, Provinsje Fryslân, Wetsus, Water Campus Leeuwarden, Voltea, IACIS and ISE for enabling this conference.

The international IAP advisory board and the local IAP2014 organization committees wish that this conference will be an opportunity for all participants to share fruitful discussions, in Leeuwarden.

Conference chairs

Prof. Dr. David Waite (University of New South Wales, Australia),
Dr. Bert Hamelers (Wetsus, The Netherlands)

Mayor Ferd. J.M. Crone of the City of Leeuwarden, capital of the province of Fryslân:

Welcome to Leeuwarden, the European Capital of Culture 2018!
Leeuwarden is a dynamic city which is situated in a green and water-rich environment.
The city has a watery heart and a heart for water.
The abundance of water is a defining feature of the city's image and atmosphere. The recovery of water, energy, food and resources has a high priority. In addition, water is an important factor in the research and development of water technology and sustainability. The expansion of the Water Campus Leeuwarden is a good example of this.
I wish you an interesting congress and enjoy your visit to Leeuwarden, the Capital of Water Technology.

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In case you have questions about general issues, the local organizing committee can help you.
During the conference you can contact them the following ways:
- ask the committee members in person;
- go to the information desk of De Harmonie;
- send an e-mail to iap2014@wetsus.nl (we will answer your mail during the conference);
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Frontpage courtesy J. de Valença “Dynamics of micro-vortices in ion-exchange membranes”

Keynote

Applications of electrosorption systems for waste water recovery

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Electrosorption Technology has been developed in dealing with the water shortage problem of the world. It has been found that the electrosorption technology is suitable for the desalination treatment of difficult waters such as waste water and mine water, due to its robust nature and low energy as well as chemicals consumptions. Several large scale industrial applications of electrosorption technology were investigated in this presentation. Various waste waters from chemical plant, steel mill, petrol refinery and coal mines as well as municipal sewage plant were treated with electrosorption technology and regenerated as fresh water supplies for corresponding industries, at capacities of 0.6 to 3.5 million gallons per day. Satisfactory continuous operations have been achieved for duration of 2 to 5 years with relatively lower power consumption and zero chemicals consumption. Studies on the real operations and laboratory experiment have shown that the deionization effectiveness of electrosorption technology is determined greatly by electrode material properties and surface oxidation status as well as cell configurations.

Keynote

Continuous performance of double-layer technologies for water desalination and energy harvesting using flow electrodes

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Capacitive technologies, such as capacitive deionization[1] and energy harvesting based on mixing energy ("capmix" and "CO_2 energy"),[2] are characterized by intermittent operation: phases of ion electrosorption from the water are followed by system regeneration. From a system application point of view, continuous operation has many advantages, to optimize performance, to simplify system operation, and ultimately to lower costs. In our study, we investigate as a step towards second generation capacitive technologies the potential of continuous operation of capacitive deionization and energy harvesting devices, enabled by carbon flow electrodes using a slurry based on conventional activated carbon powders.[3] We show how the water residence time and mass loading of carbon in the slurry influence system performance. The efficiency and kinetics of the continuous salt removal process can be improved significantly by optimizing device operation, without using less common or highly elaborate novel materials. We demonstrate, for the first time, continuous energy generation via capacitive mixing technology using differences in water salinity, and differences in gas phase CO_2 concentration. Using a novel design of cylindrical ion exchange membranes serving as flow channel, we establish the ability to continuously extract energy from available concentration differences that otherwise would remain unused. These results may significantly contribute to establishing a sustainable energy strategy when implementing energy extracting for sources such as CO_2-emissions from power plants based on fossil fuels.

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Keynote
Capacitive deionization based on flowable electrodes

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Recently, suspension electrodes ('flowing electrodes') have emerged as a mode for achieving high capacity and scalable systems for a range of infrastructure-level challenges (Fig 1a). The core idea behind flowing electrodes is that the active material (e.g. carbon) can adsorb ions *and transport/store electrons* to and from electrodes via percolation networks (Fig 1b). Thus, the physical attributes of these percolation network plays a large role in the performance of these systems (desalination/energy storage/generation/electrolysis). Furthermore, the dynamic nature of pumping a suspension in order to charge (adsorb ions) or discharge (desorb ions) charged particles is the defining difference between suspension electrodes and film electrodes. The physical make-up of the composite suspension electrodes, in terms of weight %, active material size and shape, and rheological principles are critical in order to understand the performance of a suspension electrode system.

In this talk we highlight the material science aspects of suspension-type electrodes that make it possible to eke the best possible combination of electrochemical properties in terms of long term cyclability and electrosorption capacity. Furthermore, capacitive suspension electrodes are introduced as a mode for removing ions from sea or brackish waters. We describe several key aspects toward the design and function of capacitive suspension electrodes in terms of enhancing the rheological, electrochemical, and kinetic aspects of these composite-type electrodes.

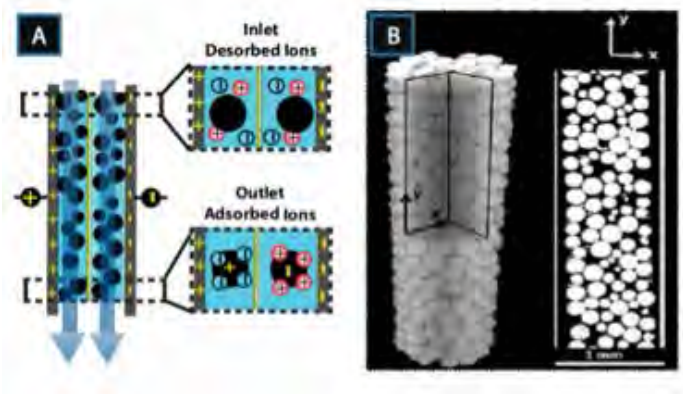

Figure 1 (a) Flowing electrode (adsorption occurs at the outlet), and XCT of percolation networks of contact points between carbon active materials.

Keynote
Water desalination by capacitive deionization - Advantages and limitations

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Capacitive deionization may serve as energy efficient method for salt removal from brackish water (<5000ppm). However, capacitive deionization may have advantages over other competitive desalination methods. One advantage introduced here is what we call "selective desalination". Since the salt is electro-adsorbed onto activated porous carbon electrode, the pores could be designed by applying a CVD process to be in a shape which doubly charged ions like magnesium and calcium ions, which are important nutrients, could not be electro-adsorbed while sodium ions could be removed selectively from aqueous solutions. In this way we can retain the magnesium and calcium ions in the feed desalinated water. Another advantage is the possibility to remove boron from water in one stage by exploiting the pH changes which occur nearby the negatively charges electrode due to surface reactions or water reduction at the cathode side, in order to transfer boric acid (which is the dominant form of boron contamination in water at neutral pH) into borate ion which could be electro-adsorbed onto the positively polarized electrode.
We also addressed one of the main limitations of the capacitive ionization method which we call herein the "Rocking Chair" problem. We are able to calculate the amount of cation and anion adsorbed/desorbed onto/from the high surface area carbon fiber electrodes as a function of the potential difference applied. It was revealed that the amount of counter-ions and co-ions electro-adsorbed onto the activated carbon electrodes are equal from both sides of the PZC at potentials in the range of about 150mV. As a consequence, it was recommended to work at narrow potential domains , i.e. the capacitive deionization cell should not be completely discharged to 0 volt, but rather to higher potentials (subject for optimization). By this approach, we were able to demonstrate high charge efficiencies in CDI based desalination processes but on the account of the salt removal capacities per charge-discharge cycle.

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Keynote

Carbon Nanofiber and Graphene Composites made by Electrospinning for Capacitive Deionization

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Capacitive deionization technology (CDI) is of great potential as an effective approach to removing salt ions from salted water. One of the challenged issues is the fabrication of high performance electrodes. In this talk, we will report a novel strategy for fabrication of activated carbon nanofiber/reduced graphene oxide (ACF/RGO) composite materials by electrospinning, followed by CO2 activation treatment at 800 oC. The morphology, mechanical property and conductivity of the electrospun ACF/RGO electrode materials were examined, and the NaCl removal capacity of ACF/RGO electrodes was tuned by changing the graphene ratio. The electrospun nanofibers have two functions: a decorating agent for immobilization of graphene and a substrate to prevent the agglomeration of graphene. The incorprated graphene helps to improve the conductivity and the pore size distribution of the ACF/RGO electrodes, evidenced by the results that the ACF/RGO-10 has an electrosorption capacity of 9.2 mg g-1, which is the highest among the ACF/RGO composites fabricated under the conditions.

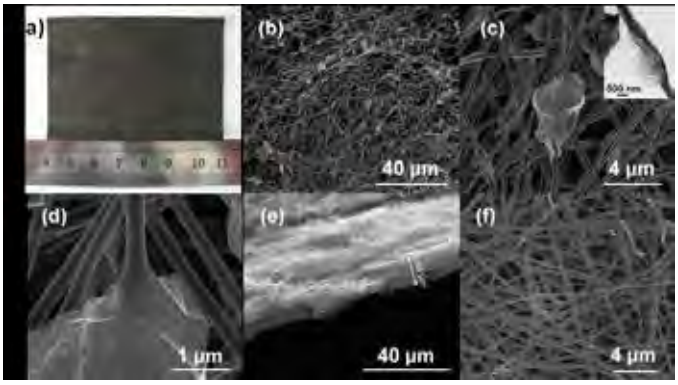

Fig. 1 (a) Photo of ACF/RGO-10, (b)-(d) SEM images of ACF/RGO-10, inset in Fig. 1(c) is the typical TEM image, (e) Side-view SEM image of ACF/RGO-10, and (f) SEM image of ACF

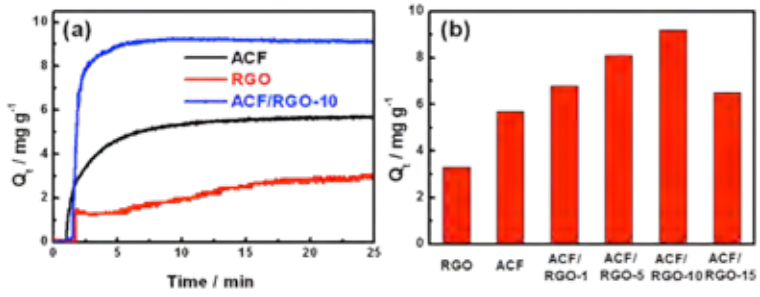

Fig. 2 (a) The NaCl electrosorption capacity of ACF, RGO and ACF/RGO-10 electrodes vs. time in CDI; (b) the desalination capacity of ACF, RGO and ACF/RGO-X (X stands for the weight ratio of RGO in the electrodes), for which the test conditions are Vcell :1.2 V, VNaCl:30 mL, and C0:400 mg L-1

Effect of pore size and its dispersity of porous carbon on capacitive deionization

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Porous carbons continue to dominate the field of capacitive deionization (CDI) for good reasons: it is an abundantly available resource with low or moderate costs yielding a high CDI performance. All electrodes used for CDI are porous at various length levels and even per se non-porous carbons (e.g., carbon nanotubes) show a large pore volume comprised from the space between particles; thus, it is of high importance to consider the total pore volume (inter- and intraparticle porosity) and its impact on the resulting CDI performance. In particular, we will review the importance of porosity measurements, the pitfalls of applying deconvolution algorithms to conventional sorption analysis data, and novel strategies to develop predictive tools for CDI sorption capacities and kinetics.

Recently, studies on microporous carbon gave convincing evidence that pores smaller than 2 nm are of high importance for the electroadsorption capacity of salt in CDI electrodes.[1] This has been a change of paradigm: before, it was believed that rather larger pores, so called mesopores (2-20 nm), are beneficial for CDI capacity.[2] New results by us, employing model carbons with precisely tuned porosity, however, show that micropores contribute to much higher degree to the salt sorption capacity compared to mesopores.[3] We used our novel nanoporous carbons to establish a predictive tool: based on cumulative pore size distributions, we were able to predict at 1.2 V and 5 mM salt concentration the salt electrosorption capacity of a large array of carbon materials in the literature. In a second step we also used a two-dimensional transport model to predict the sorption kinetics and to evaluate the optimum electrode material compaction level for salt electrosorption.

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Preparation of a MnO_2/Carbon Composite Electrode for Electrosorptive Removal of Heavy Metal from Water

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It has been believed that the physical properties and the structure of electrode materials dominate its electrosorptive performance. Manganese dioxide (MnO_2) has been extensively studied as an effective absorbent to remove heavy metals from water. Meanwhile, MnO_2 is a promising electrode material for electrochemical supercapacitors because of its high specific capacitance, good cycle stability, low cost, eco-friendly nature and abound availability. MnO_2/carbon composite materials show great potential as electrodes for electrosorptive removal of contaminant ions from water. Yang et al.[1] synthesised MnO_2/nanoporous carbon composites and successfully used them as electrode in capacitive deionization technology. In addition, MnO_2/carbon materials composite showed great adsorption ability to remove heavy metal ions from waste water [2, 3]. Although MnO_2 is an effective absorbent for many metal ions and a promising electrode material for electrochemical supercapacitors, no previous study combines the two properties and uses it as electrode to remove metal ions by electrosorption process.

In the present study, a simple and cost-effective electroplating approach was used to directly deposit a thin MnO_2 layer on the surface of carbon cloth (CC). Morphology, structure, and capacitive properties of the prepared MnO_2/CC electrode were characterized. On the basis of the materials characterization, we evaluated the electrosorptive performance of the MnO_2/CC electrode on Cu^{2+} and Pb^{2+} removal. The scanning electron microscope images clearly showed the film of nano MnO_2 clusters on CC surface. With increasing deposition time, the thickness of nano clusters gradually increased. An XRD pattern for the MnO_2/CC electrode indicated a long-range disorder of MnO_2 in these composites. Electrochemical characteristics of the MnO_2 /CC electrodes prepared for different deposition periods were evaluated by using cyclic voltammetry (CV). The voltammetric current response, and consequently the capacitance of the coating, increased substantially with increase in deposition time from 500s up to 7200s. The capacitance, however, it calculated that deposition time of 1000s was optimum for achieving maximum capacitance and the capacitance was as high as 380 F/g. The MnO_2/CC electrodes showed high efficiency on electrosorptive removal of Cu^{2+} and Pb^{2+} from water. Voltage, pH, and the amount of loading MnO_2 significantly influenced the electrosorption performance in Cu^{2+} and Pb^{2+} removal.

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Zinc oxide nanorods coated carbon electrodes for improved energy efficient capacitive desalination of brackish water

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Capacitive deionization (CDI) with its low energy consumption and capital costs accompanied with a smaller footprint and portability is catching recent attention worldwide, especially for desalting brackish water. It works on the principle of electric field mediated ion adsorption in the electrical double layer (EDL) formed at the electrode surface upon the application of an external potential. Symmetrically assembled activated carbon cloth (ACC) electrodes having a high surface area can increase the ion adsorption capacity, increasing the salt removal efficiency of the system. By coating the ACC surface with a dielectric material like zinc oxide nanorods (ZnO)[1], we were able to increase charge efficiency of the composite electrode by 20%, attributed to increase in capacitance of the electrode. Uniform electric field distribution at the ZnO nanorods surface increased the ion adsorption and desorption rate at the electrode surface, increasing the salt removal efficiency by 45%. Faster ion transfer rates also contributed to reducing the desalination and regeneration times by an average of more than 50%, leading to a net power consumption of less than 25 mW per adsorption cycle. The reduction in regeneration time led to a reduction in the overall water wastage during the process thus improving the recovery rate. The electrodes were characterized for active surface area, capacitance from cyclic voltammetry curves and theoretical assessment of surface area utilization and magnitude of electric field force acting on an ion of unit charge for an applied potential. Some results on larger electrode sized capacitive desalination prototype will also be discussed.

References

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Removal efficiency of high concentration waste water using Capacitive Deionization Process

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The volume of usable fresh water has been decreasing globally due to pollutions of river and underground waters. The pollution of underground water, resulted from phosphate and nitrate ions, eutrophicated. For the prevention of these problems, the need to disposal of nitrate and phosphate ion is currently growing day by day. This study is to confirm ion adsorption properties of nitrate ions and phosphate ion in high concentrate-synthetic waste water by using CDI(Capacitive Deionization) process.

CDI cell was fabricated to confirm ion adsorption properties, and synthetic waste water made of 5,000ppm NH_4-N, 4,000ppm NO_3-N, 3,000ppm PO_4-P is used. In experiment method, batch type of charging 1 minute and discharging 3 minutes proceeded after inflow of synthetic waste water into CDI cell. Charging and discharging as 1 cycle, 40 cycles proceeded, and then treated waste water which drained out from discharge process analyzed with sampling.

This study researched on ion adsorption properties for elimination of nitrate and phosphate ion in high concentrate-synthetic waste water using CDI process. As a result, it was confirmed that NH_4-N, NO_3-N, PO_4-P are respectively 79.61%, 72.10%, 73.97% adsorbed.

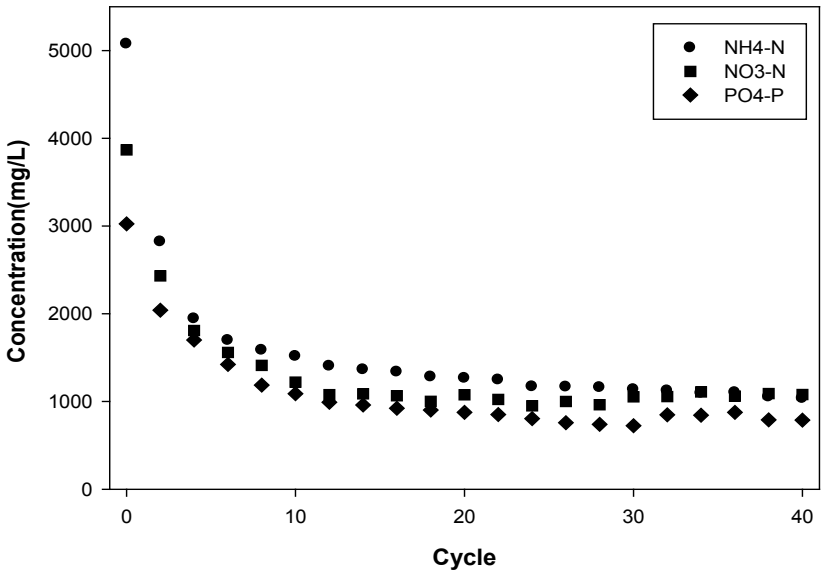

Figure 1 Variation of NH_4-N, NO_3-N, and PO_4-P concentration during the adsorption

Batch mode and continuous membrane capacitive deionization using flowing carbon electrodes

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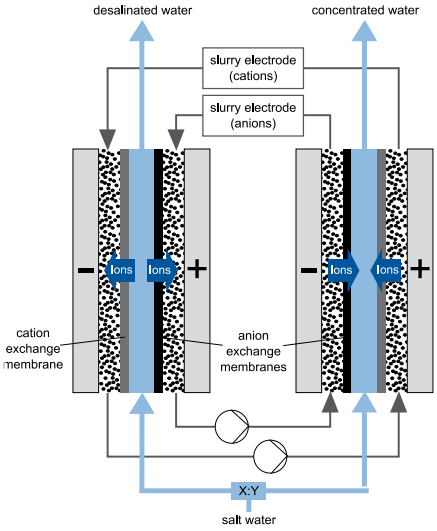
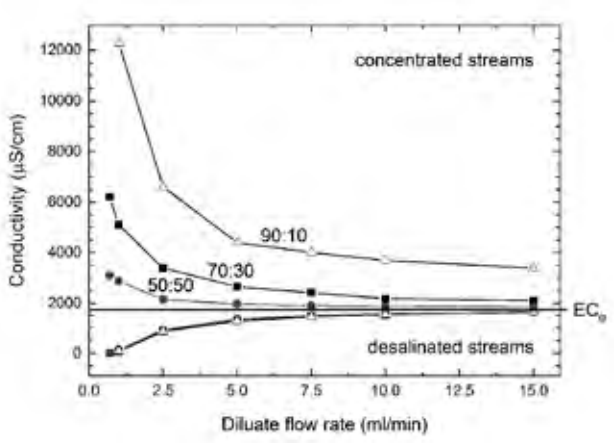
Continuous water desalination using Membrane Capacitive Deionization (MCDI) process assisted with flowing carbon electrodes is reported. Batch-mode experiments showed extremely high salt adsorption capacities of 260 mg/g for the flowing activated carbon electrodes. A continuous process comprised of desalinating and concentrating MCDI units and two recirculated flowing electrodes was operated at 50, 70 and 90% feed water (1gNaCl) split ratios. Desalination rates of more than 99% were achieved at > 90 % water recovery, and were independent on the diluate/concentrate flow rate ratio.





Hyper Salinity Desalination using Atlantis RDI Capacitive Deionization Technology

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Atlantis Technologies has developed the next generation capacitive deionization technology that enables the practical desalination of industrial waste water exceeding 100,000 mg/l salinity. The technology was developed in California for use on industrial waste waters such as oil/gas produced water, supersaturated mining water, and flue gas desulfurization waters generated by coal fired power plants. This is possible through dramatically increased flux rates, extended capacitors flow lengths, and unique system operation which together increase the range of applications by a factor of 10 - 20. Our presentation will showcase lab and field studies, flux rate characterizations, and system design.

Capacitive Deionization for Waste Water Re-use: Energy Efficiency Considerations

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Due to the always increasing worldwide water scarcity associated to the climate change there is the need to increase the reinjection of wastewater into the overall water cycle. The reuse of treated waste water has been identified as a potential way for addressing long term imbalances between water demand and water supply, therefore reducing the vulnerability of water and environmental resources to climate change and man-made pressures. This study provides a mechanistic analysis of Capacitive Deionization (CDI) applied on Waste Water Re-use, paying special attention to Energy Efficiency aspects. CDI technology is gaining increased scientific interest since 2006 [1]. However, not too many publications indicate the feasibility of the kWh/m3 consumption in CDI systems. The common assumption proposes that the main problem may be the ions adsorption capability of the electrode material during charging [2]. To our experience, desorption processes may be even more problematic, in energy efficiency terms, since they hold diffusional difficulties when submitted to relatively high current densities [3].

This work provides an overview of current strategies for operating these systems aiming to improve energy recovery and lead this process to the point of making these systems an option for use in waste water treatment plants. Experimental work includes consecutive deionization – regeneration tests conducted under a combination of constant current and constant voltage steps at different current rates (close to real life scenarios). A schematic representation of the performance profile proposed can be seen in Figure 1 (left) [4].

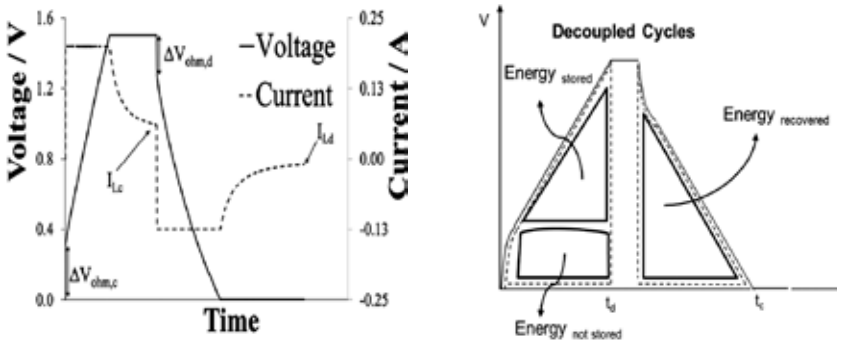

Figure 1 Charge-discharge configuration in decoupled procedures (left). Energy components in decoupled cycles (right). [4]

As result, in order to further optimize efficiency in the CDI process, particularly for 2 000 – 20 000 ppm waste water concentration, we are systematically improving strategies for operating these systems in such a way to achieve major impact on the practical application of this technology [4].

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Ion adsorption at mineral-electrolyte interfaces probed by high resolution Atomic Force Microscopy

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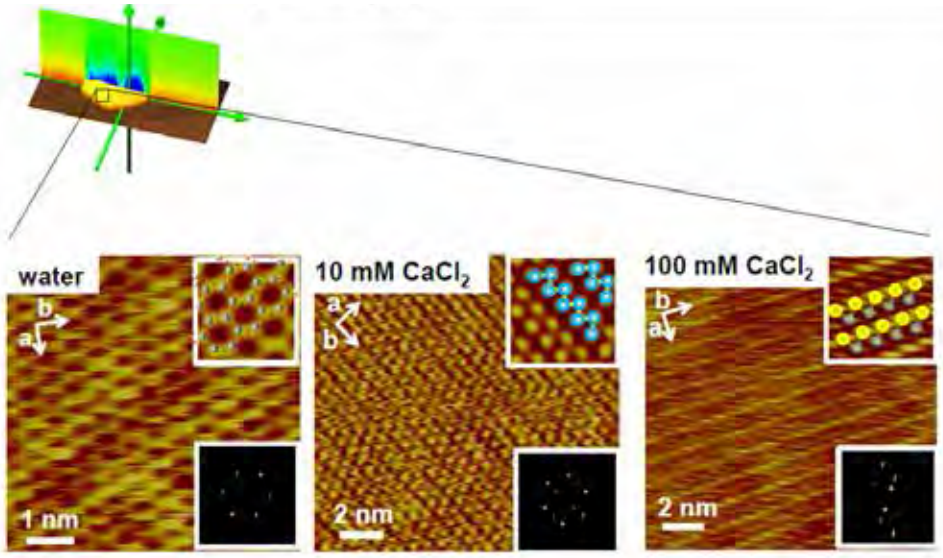
The distribution of ions and charge at solid-water interfaces plays an essential role in a wide range of processes in biology, geology and technology. While theoretical models of the solid-electrolyte interface date back to the early 20th century, a detailed picture of the structure of the electric double layer has remained elusive, largely because of experimental techniques have not allowed direct observation of the behaviour of ions, i.e. with subnanometer resolution. We have made use of recent advances in Atomic Force Microscopy (AFM) to reveal, with atomic level precision, the ordered adsorption of the mono- and divalent ions that are common in natural environments to heterogeneous gibbsite/silica surfaces in contact with aqueous electrolytes. Complemented by density functional theory, our experiments produce a detailed picture of the formation of surface phases by templated adsorption of cations, anions and water, stabilized by hydrogen bonding. In particular, we demonstrate the sequential build-up of the Stern layer by consecutive adsorption of Ca^{2+} and Cl^- ions upon increasing the bulk concentration of $CaCl_2$. Simultaneous measurements of the charge in the diffuse layer using AFM spectroscopy suggest that deprotonation of hydration water largely compensates the charge due to cation adsorption.



Pore-scale study of processes and transport in porous media; an overview

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To increase our insight of flow and transport phenomena in porous media on both micro- and macro scales, pore-scale studies are essential. Studies have included chemical, biological, and physical applications. Experimentally, micro-models have been proven to be a valuable tool as they allow the observation of flow and transport phenomena on the micro-scale. A micro-model is an artificial representation of a porous media, made of a transparent material. We have used Poly-Di-Methyl-Siloxane (PDMS), which is a viscoelastic, silicon-based organic polymer. It is optically transparent, inert, non-toxic, and non-flammable. We have performed two-phase flow and colloid transport experiments in these micro-models. We have established that the inclusion of fluid-fluid interfacial area allows for the modelling of the hysteretic relationship between capillary pressure and saturation in porous media. In other words, data points of capillary pressure-saturation-interfacial area from many (scanning) drainage and imbibition experiments fall on a single surface. In colloid transport experiments, we directly observe colloids movement, their retention at interfaces between phases, and their mobilization by moving interfaces and contact lines.
Another valuable tool is pore-scale modeling, which allows us to conduct numerical “experiments”, from which closure equations for macro-scale description can be obtained. Currently, we are using a Discrete Element Method to study the coupling between swelling porous media and pore fluid flow.

The Dynamics of Micro-vortices During Overlimiting Electrodialysis

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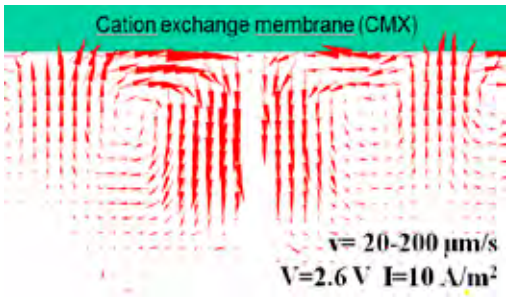
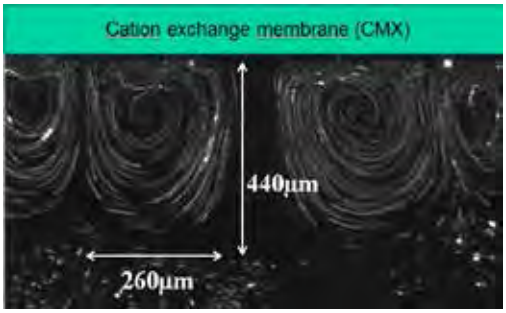
We experimentally investigate the coupled dynamics of global ion-flux and local hydrodynamics of an electrolyte solution close to a charge selective membrane under an electric forcing. At small voltages, cations transport diffusively across a cation exchange membrane (CEM), whereas the transport of oppositely charged anions is blocked, causing the main resistance of the system. At higher voltages this resistance suddenly increases and in addition to diffusive transport, hydrodynamic convection sets in within a boundary layer of O(100 µm), resulting in the so-called over-limiting current. In this regime we measured the fluid flow with particle image velocimetry (PIV) combined with chronopotentiometric resistance measurements for the first time. Our results reveal that the micro-vortices are caused by gravitational unstable gradients and by electro osmotic-coupling between the membrane surface and the solution. Moreover, under a constant applied electric current, the electroconvective micro-vortices start with a voltage jump and grow linearly both in size and speed. After this initial linear growth, the resultant voltage levels off around a fixed value. The average vortex size stabilizes as well, however the individual vortices are unsteady and dynamical. Our experimental setup and results offer a complete picture of the coupled dynamics of the hydrodynamics and electrical responses of an electrolyte, beneficial for characterizing a variety of charge selective membranes in order to improve electrodialysis desalination processes.





Water Purification and Brine Concentration by Shock Electrodialysis

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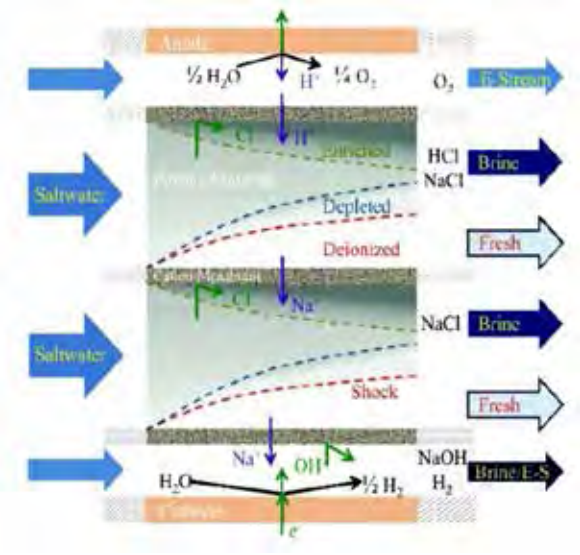
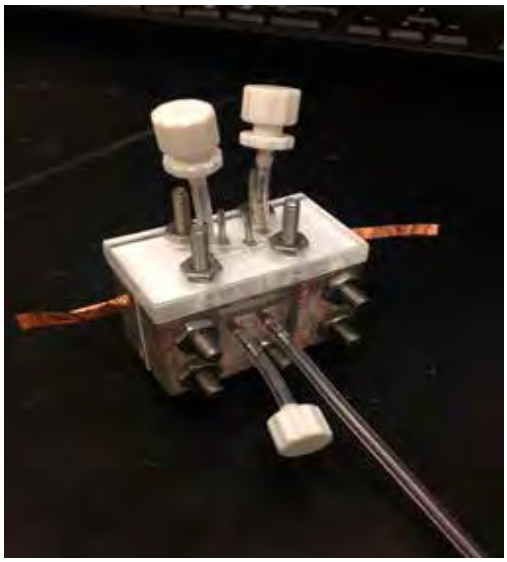
In this project, we investigate experimentally and theoretically the possibility of exploiting deionization shocks in porous media for water purification and brine concentration by "shock electrodialysis". The basic idea of this new approach is to drive an over-limiting current (faster than diffusion) through a charged porous medium sandwiched between two cation-exchange membranes, perpendicular to a pressure-driven cross flow, which produces a sharp "shock" in the salt concentration profile between deionized and concentrated steams, which are separated at the outlet. In contrast to classical electrodialysis, only one membrane type is needed to trigger the phenomenon, and the separation is effectively "membraneless" within the porous medium. Boundary layer analysis, generalizing the Leveque solution for over-limiting current, provides useful engineering principles, and detailed simulations of the system help us gain insight into the phenomena at play. We demonstrate the principles of shock ED experimentally in a sequence of prototypes. Initially we use copper electrodes and copper sulfate solution to demonstrate the feasibility of the project and then replace the copper electrodes with electrode streams sustaining the current by water electrolysis, as in traditional ED, in order to be able to use this phenomenon to remove a wide range of electrolytes, including sodium chloride, from water. The results show reasonable efficiency and unique separation capabilities, such as removal of particles and disinfection, that may find applications in compact water treatment and brine concentration.





TEMPERATURE EFFECTS ON ENERGY PRODUCTION BY SALINITY EXCHANGE

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In recent years, the capacitance of the interface between charged electrodes and ionic solutions (the electrical double layer, EDL) has been increasingly investigated as a source of clean energy from salt concentration changes [1-3]. Charge is placed on the electrodes either by means of ion-exchange membranes (CDP or Capacitive energy extraction based on Donnan Potential) or of an external power source (CDLE or Capacitive energy extraction based on Double Layer Expansion). In the latter method, net energy is produced by simple solution exchange in open circuit (Fig. 1),. In this communication, we propose to explore the changes in capacitance associated to temperature variations as well: a temperature increase produced a decrease in EDL capacitance and hence a cycle is possible in which some charge is put on the electrodes at a certain potential, and returned at a higher one (Fig. 1). There is also the possibility of gaining energy from the so-called thermal membrane potential: an electric potential is generated when hot and cold waters are contacted with anion and cation exchange membranes, respectively [4]. DLE technique from the exchange of cold and warm waters (double layer permittivity exchange, DLPE) successively in contact with charged electrodes. Furthermore, we will demonstrate, both theoretically and experimentally, that temperature and salinity variations can be suitably combined (charging the electrodes in cold sea water, and discharging them in warm fresh water) to maximize the potential increase and the energy available.

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Acknowledgements

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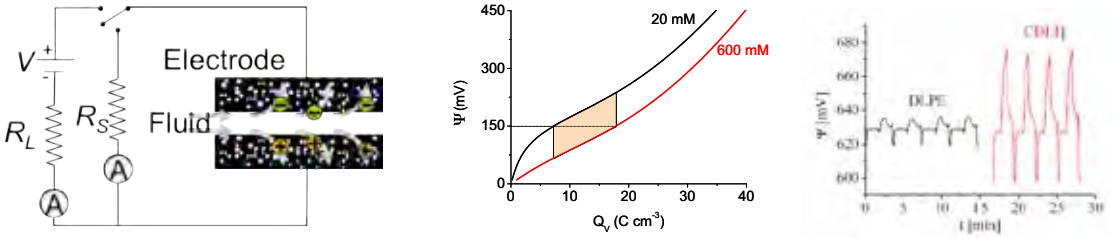

Figure 1. Left: The CDLE process; center: a typical charge-discharge cyle; right: DLPE and CDLE compared in experimental conditions. Here we demonstrate that it is feasible to gain net energy in the C

Functionalized activated carbon for “capacitive mixing” energy production

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The “capacitive mixing” (CAPMIX) technique for the energy production can be considered the reverse of CDI. In the simplest case, the so-called “capacitive double layer expansion” (CDLE) technique, we exploit the increase of the electrostatic energy of an electric double layer, that takes place when the concentration of the solution is reduced, resulting in the diffusion of the ions against the electric force. The electric double layers must be already present when the concentration is changed; they are usually generated by charging the electrodes by means of an external power supply. Now we report experiments in which the double layers are obtained by chemical means: charged functional groups are added to the surface of the activated carbon. This leads to the spontaneous formation of an electric double layer, without the need of an external device for charging the electrodes. We show that this approach leads to stable and repeatable performances of the electrodes, with a power production of the order of 100 mW per square meter of electrode.

Ultrathin metal oxide coated mesoporous carbon material for enhanced capacitive deionization

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

Mesoporous carbon nanofiber fabrication and its capacitive desalination application

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The lack of fresh water is one of the most serious problems for human beings in the 21st century. In order to generate fresh water from sea water and brackish water, various desalination methods, such as distillation, electrodialysis, reverse osmosis, activated carbon adsorption and ion exchange method have been developed for water desalting. Capacitive deionization (CDI) technology is recently becoming increasly attractive as an alternative desalination method due to low energy consumption and needless of chemicals[1-2]. CDI is referred to an electrosorption process, in which ions in water are adsorbed in the electrical double layer when electrodes are charged, and then desorbed when electrodes are discharged. At the same time, the electrode is regenerated. Because the voltage applied between the positive and negative electrodes in CDI cell is lower than that of water electrolysis(< 1.2V), water electrolysis is avoided and much energy saved[3]. Therefore, it is a very promising technology for water desalination nowadays.

The high capacitive and high conductive electrode materials are needed in order to enhance the accumulation of ions and decrease energy consumption, respectively. A high capacitive material should have a high surface area for ion accumulation. Recently, the high porous and conductive carbon based materials, such as carbon aerol gel[2], carbon nanotube[4] and carbon fiber[5] have been developed in order to increase the desalination capacity of the electrode materials.

Electrospun technique is very suitable for carbon nanofiber material fabrication with 100-500nm diameter[6]. The electrostatic force between the tip and collector electrode drives the fiber formation of a polymer solution. One of the most used polymer is polyacrylonitrile (PAN) due to its good spinnability in solution[7] and its relatively high carbon yield.[8] The resultant PAN-based carbon fiber has high surface area and tunable porous structure after suitable activation by steam activation or CO2 activation[9]. These physical activation processes were difficult to control the pore size and the porous carbon fibers were easily deactivated with recycling. In this report, we present our strategy to get the self-sustainable mesoporous electrospun carbon fiber by adding some chemicals such as polymethyl methacrylate (PMMA) or polystyrene (PS) in the electorspun polymer precursor solution as a pore-forming component. BET analysis, SEM and electrochemical characterization were made to understand the porous structure and capacitive properties. The pore size and density can be tuned by adjusting the ratio of the additives. The mesopores with 10-50 nm pore size were formed at the ratio of PAN/PMMA of 4:1. Cyclic voltammetry experiment confirmed that the specific capacitiance of the carbon fiber has a significant increase compared with the pure PAN drived carbon fiber. The capacitive desalination performance was investigated by assemblying the self-sustainable mesoporous fiber electrode in the capacitor. The salt adsorption capacitance was 6.5 mg/g and 7.5 mg/g corresponding to PAN/PS and PAN/PMMA drived carbon fiber electrode, respectively. Both are much higher than that of the pure PAN drived carbon fiber (2.3 mg/g). The stability test was measured. It demonstrates that the mesoporous carbon fiber electrode is potential for water softing and brackish water desalination application.

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CDI carbon electrode coated with ion selective layer

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Capacitive deionization (CDI) is an ion removal technology based on storing ions in the polarization layers of two oppositely charged electrodes. CDI process is defined as a potential driven adsorption of ions onto a charged electrode surface. CDI is a technology similar to that of electric double layer (EDL) super-capacitors but modified to operate in a flow through system. Conventional CDI is known to be energy inefficient because of the dissolved salt present in the pore volume of the carbon electrode. When an electric potential is applied, counter-ions in the pore adsorb onto the electrode and co-ions are expelled from the electrodes. So ion adsorption and desorption occur simultaneously in the surface of electrode, seriously reducing desalination efficiency. To solve this problem, a charge barrier should be placed near to the electrode of CDI[1]. It is called membrane-capacitive-deionization (MCDI) in which very expensive ion exchange membranes are used. So, we have developed novel CDI electrode coated with very thin ion exchange layer, which is shown in the Fig. 1. This CDI electrode leads to have very low resistance, to enhance the salt removal performance and to lower its production cost[2].

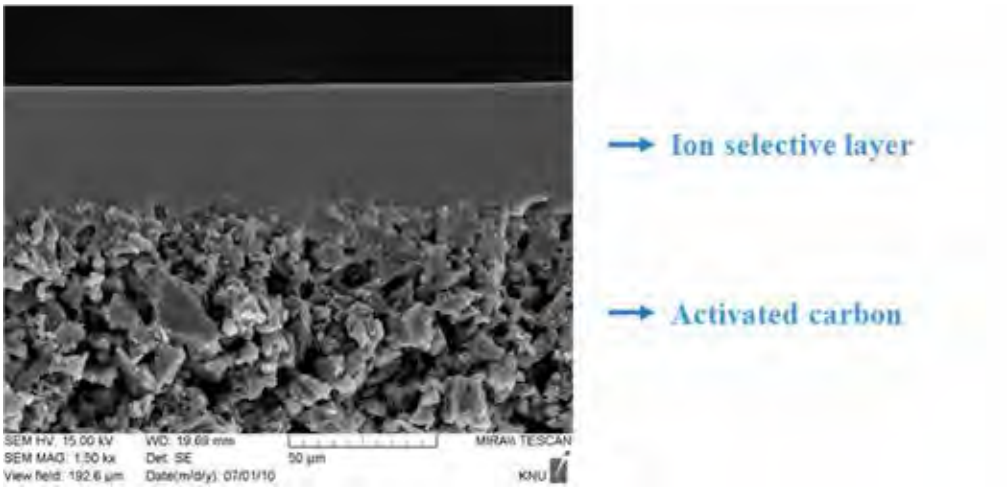

Fig. 1. SEM image of the cross section of ion selective layer coated CDI electrode.

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Keynote

The Importance of Carbon Electrode Material Affecting the Maximum Deionization Performance in CDI Process

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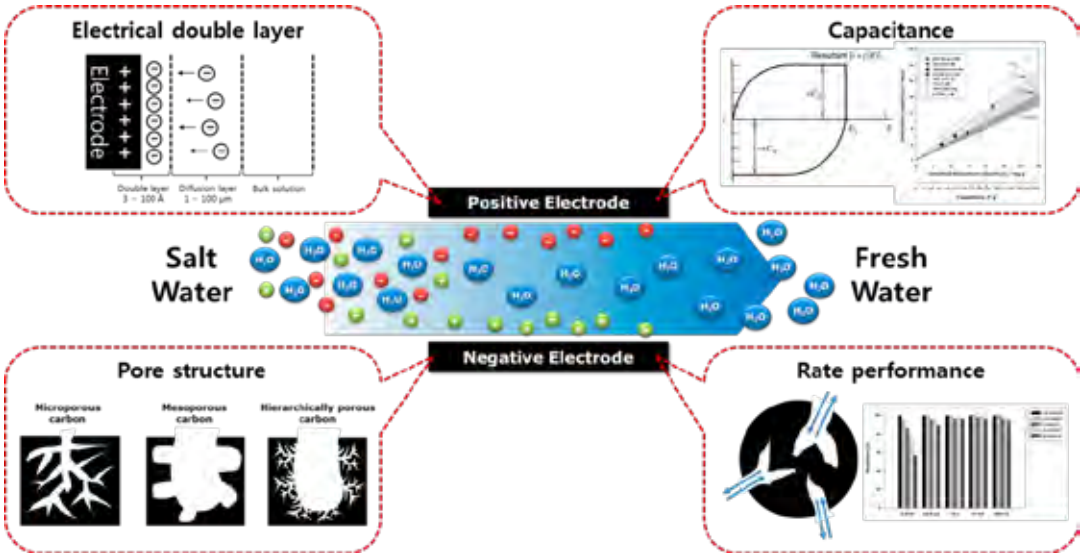
Water shortage problem is a global environmental issue today. Desalination can provide a solution to water scarcity and subsequent increasing freshwater demands in agriculture, industry, and household. Recently, capacitive deionization (CDI) has attracted growing attention as a novel desalination technology. CDI produces deionized water while saline water passes between closely-packed electrodes upon charging, in which porous carbon materials play an important role to achieve an effective desalination. Therefore, various carbon materials, such as carbon aerogel, ordered mesoporous carbon, and carbide-derived carbon, have been investigated as CDI electrodes to provide improved desalination performance. Previous studies have reported that the desalination performance in terms of deionization capacity (or salt adsorption capacity) was significantly affected by types of carbon material. In this presentation, we will show how importantly the deionization performance is affected by carbon electrode materials including their deionization capacity, especially focused on properties of carbon electrodes.



Insight into the electrochemical property of TiO_2/AC electrodes prepared by a microwave-assisted ionothermal synthesis method for capacitive deionization

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Four nanostructured anatase titanium dioxide (TiO_2)/ activated carbon (AC) composite materials for capacitive deionization electrodes were prepared by a two-step microwave-assisted ionothermal (sol-gel method in the presence of ionic liquid) synthesis method. It includes a reaction and a crystallization step. In the crystallization step, the ionic liquid plays a hydrothermal analogy role in driving the surface anatase crystallization of amorphous TiO_2 nanoparticles formed in the reaction step. The electrochemical property of these composite electrodes was investigated.

In general, the electrode prepared from the AC material with highly hydrophilic surface would have high specific capacitance. It was also reported that the specific capacitance of activated carbon electrode was enhanced after the modification of nanostructured anatase titanium dioxide. However our results found out that the effect of TiO_2 on the specific capacitance of nanostructured anatase TiO_2/ AC composite is dependent on the characteristics of pristine AC, especially for the pore size and the hydrophilicity in our study system. It may be a positive effect or negative effect. The negative effect was observed in the case of AC material with micropores and highly hydrophilic surface. These effects will be investigated and discussed using multiple techniques, including X-ray spectroscopy, thermogravimetry analysis, cyclic voltammetry, electrochemical impedance spectroscopy, etc.

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Vertically-Aligned Carbon Nanotube Electrodes for Capacitive Deionization

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We investigated the role of porous geometry using vertically-aligned carbon nanotube (VA-CNT) electrodes in capacitive deionization (CDI). CDI promises to be an efficient and compact means to achieve water desalination through adsorption of ions on high surface area electrodes. In order to optimize salt adsorption in CDI, an improved understanding of electrode properties, such as optimal pore size and electrode thickness for ion removal [1], is desired. Current studies typically use highly porous, tortuous electrode materials, which complicates the ability to obtain detailed understanding of salt adsorption and charging dynamics. In this work, we designed and synthesized VA-CNT electrodes to investigate the role of height and spacing on salt adsorption rates. The VA-CNTs were synthesized using chemical vapor deposition with inner and outer diameters of 5.6 nm and 7.7 nm, respectively, and heights of 20 to 600 µm, with specific surface areas of 540 m2/g. These VA-CNTs were transferred onto a corrosion-resistant electrode using Au-Au thermocompression bonding [2] (Figure 1). We first characterized the capacitance and charging dynamics with a three-electrode test cell in sodium chloride solution. The material capacitance ranged from 20-40 F/g in NaCl solutions of varying concentrations from 15-1000 mM, respectively. The charging time constants were extracted from the potentiostatic data (Figure 2), which indicate that the time constant varies linearly with the height of the carpet and is proportional to the Debye length. These results suggest that the charging effect is due to charge storage in the double layer and surface conduction in the CNTs. These effects may be due to the mesoporous nature of the CNT carpets. In addition, we are currently investigating the VA-CNTs in a flow through test cell, where we can correlate the results from the potentiostatic measurements to ion removal for desalination. These results offer a first step towards improved understanding of porous electrode geometries for CDI.

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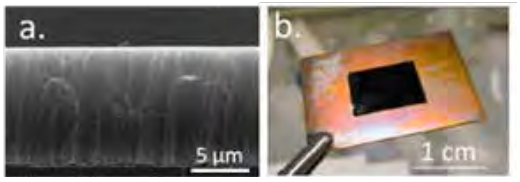

Figure 1. Synthesized VA-CNT electrodes. a) Scanning electron microscope images of transferred CNTs, b) CNT carpet transferred onto corrosion-resistant substrate.

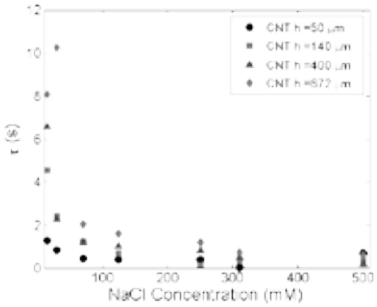

Figure 2. Charging time constant of CNT electrodes for varying heights and sodium chloride solution concentrations. Potentiostatic measurements were taken in a 3-electrode cell.

The Influence of Heteroatom Doping of Porous Carbon on the Salt Adsorption Capacity and Kinetics in Capacitive Deionization

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Key words: Porous Carbons, Salt Templating, Nitrogen-Doped, Sulfur-Doped

The production of potable, deionized water is a major challenge and capacitive deionization (CDI) has gained increased attention over the last years as an energy efficient alternative to reverse osmosis or ion exchange technologies for desalination of brackish water. Since CDI is based on the same phenomenon of ion electroadsorption as electrical double layer capacitors, porous carbons in general and activated carbons in particular are of interest and importance to CDI as they combine high surface area and low manufacturing costs with high availability. Various fabrication techniques (e.g., carbide-derived carbons, physical or chemical activation of biomass etc.) can be used to produce porous carbon materials. Especially the carbide-derived carbons are of great importance to understand the impact of the pore size distribution on the CDI process[1].

In our study , for the first time, we apply salt templated carbons for water desalination using CDI with a high surface area and pore volume derived via simple solution based bottom-up process allowing to produce porous carbons from glucose. Zinc chloride was used as a salt template to introduce porosity[2]. By careful adjusting the ZnCl2 to glucose ratio the morphology can be tuned from a microporous to a mesoporous material. The resulting carbon material can be easily doped with sulfur or nitrogen by adding soluble precursors or changing the carbon source to glucosamine. Both, the impact of these heteroatoms and the details of porosity and pore size distribution on the overall CDI performance and salt adsorption kinetics will be presented and compared with the validity of the CDI predictive tools published in Ref. [3].

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Characterization of Internal Resistance for Capacitive Deionization Systems

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Current CDI devices consume significantly more energy than the theoretical thermodynamic minimum.[1] One significant energy cost pathway is power dissipation through the internal resistance of CDI cell during charging and discharging. Therefore, understanding the contributions to resistance in CDI systems is critical for developing high performance devices. We are working to fully characterize resistive components and associated energy costs in CDI systems with the goal of reducing those resistances and developing low energy consumption devices. Internal resistance in CDI systems consists of ohmic resistance in materials, solution resistance and charge transfer resistance.[2] Figure 1 shows the resistive components in a typical CDI cell. All these components contribute to energy dissipation in charging and discharging process. We designed a custom four-probe measurement platform to measure resistivity of porous electrodes and characterize contact resistance between electrodes and current collectors under various operation conditions. We used electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge tests to perform measurements. Our characterization is based on using carbon aerogel monoliths (HCAMs)[3] as electrodes and several common carbon or metal materials as current collectors. Our preliminary results demonstrate that charge transfer resistance can be reduced by applying compression force on electrodes and current collectors (Figure 2). Other affecting parameters may include porous electrodes materials, current collector materials and feed solutions.

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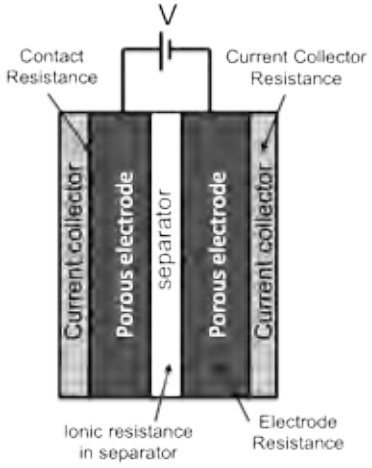

Figure 1. Resistive components in a CDI cell

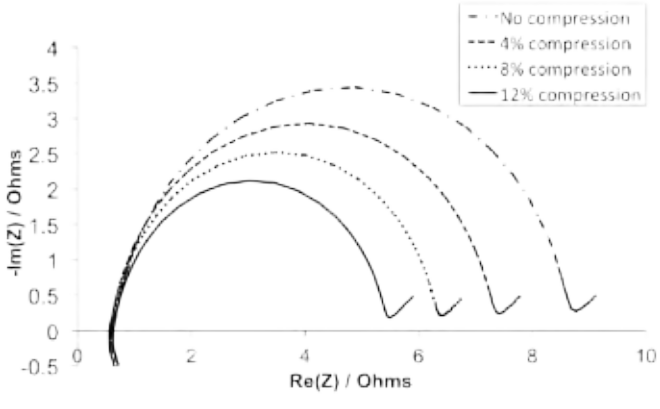

Figure 2. Reduced charge-transfer resistance by electrodes compression

Study of Electrosorption Performance of Nanostructured Carbon Electrodes in Capacitive Deionization

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Capacitive deionization (CDI), or referred to as electrosorption process, is a promising nanotechnology as a means of saving energy and producing purified water. The working principle of CDI relies on electrochemical separation of ions onto highly porous carbons, which is similar to that of energy storage in supercapacitors. It is noted that the choice of nanostructured carbon electrodes is the key factor to determine the deionization performance. The objective of this study is to identify the effect of pore characteristics on desalting capability in the CDI process. Several carbon materials with various porosities, such as carbon aerogel, activated carbon, multiwalled activated carbon, and ordered mesoporous carbon, are tested. The capacitive behaviors of carbon electrodes are evaluated by using cyclic voltammetry. Electrosorption experiments with a CDI cell are carried out to assess the deionization performance of carbon electrodes. The obtained results show clear trends in the relationship between the electric double-layer capacitance and electrosorption capacity. Also, the carbon materials possessing the different pore sizes show different types of cyclic voltammograms. One can see that the electrosorption capacity strongly depends on the specific surface area and the pore size distribution of carbon materials themselves. The carbon electrodes associated with larger mesoporosity result in a higher effective surface area and greater electrosorption capacity. The good electrosorption performance could be attributed to the presence of mesopores that are less affected by double-layer overlapping and then facilitate ion transport in the CDI process. More specifically, Grand Monte Carlo simulations (GCMC) can be further used to provide the insights into ion distribution inside charged nanopores and to predict its electrosorption capacity. The findings of this work can provide useful information to search the desirable carbon materials in CDI process.

Pore-structure of Activated Carbon Fibers on Capacitive Deionization

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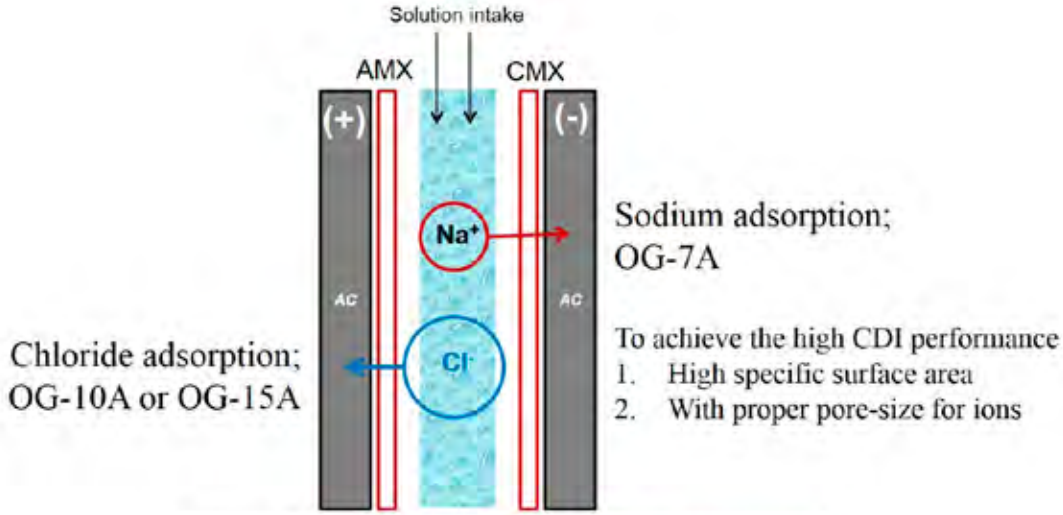
We develop the capacitive deionization (CDI) system for the purification of sodium-chloride containing water using activated carbon fibers. The pitch-based activated carbon fibers (OG-series; 7A, 10A, 15A, 20A from Osaka gas Co. Ltd. Japan) have varying degree of activation with different surface area and pore-distribution. These materials were applied in CDI system and evaluated the ion adsorption capacity of sodium/chloride respectively. The experiments were conducted at various applied voltage, solution feed rate, and concentration. The results of experiments indicate that the pore structure of OG-7A is suitable for sodium ion adsorption and OG-10A or OG-15A has adequate pores for chloride. The detailed relations between the desalination of sodium/chloride ions and pore-structure of activated carbon fiber are discussed in this presentation.



	as_{BET}/m^2g^{-1}	Wp.peak(volume)/nm	Wp.peak(area)/nm
OG-7A	861	0.6911	0.6911
OG-10A	1228	1.3036	1.0852
OG-15A	1793	1.5220	1.3036

Capacitive Deionization with PZC-Modified Carbon Xerogel: Half-Cell and System Analysis for Long-Term Operation

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Capacitive deionization (CDI) is an emerging water treatment technology that holds many benefits over existing pressurized membrane separation systems including low energy cost of separation, modular design, and possibly lower capital and maintenance costs.(1) This growing technology has not become commercially widespread for a few reasons:

1 Cost competitive carbon electrodes capable of higher salt capacities are still needed
2 Demonstration of longer equipment lifetime needs to be accomplished
3 Energy benefits of the operation need to be further shown and compared to existing reverse osmosis (RO) systems and other combined water treatment technologies
4 Marketing the technology needs to take place to interested customers in a variety of markets

In recent years, CDI has come a long way towards meeting these goals, especially with the inclusion of membranes which are capable of not only increasing the salt capacity of the electrodes, but also of enabling fast regeneration of the adsorption surface.(2, 3) While the addition of membranes is quite attractive, it comes at the cost of added complexity and the increased possibility for fouling.
An alternative to membrane capacitive deionization (MCDI) is the use of a potential of zero charge (PZC) modified carbon electrode that can increase the salt capacity of the electrode while also possibly decreasing the overall costs of the device.(4-6) These cost effective PZC-modified carbons can increase charge efficiencies by up to 50%.(7) However, the functional groups on the carbon surface will change over time as Faradaic oxidation reactions occur. These new oxide groups can substantially affect the salt capacity of the carbon electrodes and must be dealt with to maintain the separation ability of the CDI process. In the work presented here, various mitigation mechanisms will be shown that can extend the lifetime of a CDI cell by controlling the surface oxide groups and limiting the shifting of the PZC into regions that can negatively affect the electrosorption capacity and charge efficiency. Both chemical and electrochemical options will be demonstrated with cycling experiments carried out at greater than 150 cycles.

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Temperature effects on the desalination of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigated the effect that varying the temperature of the water has on the properties of blue engine and desalination cycles. Desalination cycles were found to be most effective when cold water is used. There is a ~10% decrease in required energy when changing from equatorial to arctic sea water.

Furthermore, we studied the effect of using water at different temperatures within one cycle. Saline water reservoirs at different temperatures can be obtained by e.g. pumping sea water from depths to the surface or by using cooling water from industrial facilities in an intelligent way. Desalination becomes increasingly cheap when performing the charging step in sea water of lower temperature than the discharging step. Interestingly, the characteristics of the engine (pore size, pore volume, bath volume) can be tailored such that the required energy vanishes already for small temperature differences.

These positive temperature effects on the efficiency are not at all exclusive to desalination cycles, similar temperature effects are also observed in blue energy cycles. We find that blue energy harvesting can be enhanced when fresh water is used which has a higher temperature than the sea water. For large temperature differences of the order of 50 degrees this boosts the work per cycle by a factor of two, compared to existing techniques (see figure).

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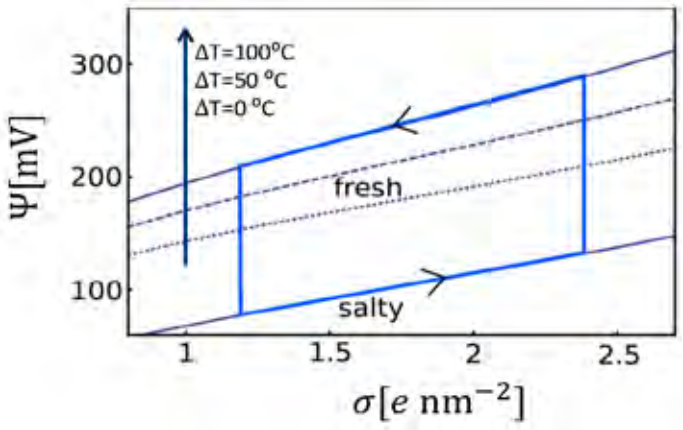

Figure: Blue energy cycle in the potential – charge representation. Stroked lines represent the upper part of the cycle, connected to fresh water reservoirs of different temperature.

Structural and size effects on the desalination cycle of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigate the effect, which varying pore and engine sizes have on the properties of the desalination cycle. To obtain comparative results, we introduce the size ratio x=Vb/(Vb+Ve) between the volume Ve of the capacitive engine and Vb of the bath, which is desalinated. By this, we compare desalination cycles, which are obtained by using electrodes, completely build of pores with a certain fixed size. We find that the size ratio x does effect the amount of energy that is needed to desalinate one liter of water; interestingly, the desalination cycle becomes optimal for very large ratios x, when the desalination bath becomes very large in comparison to the engine (see figure). Thereby, the required energy can vary by more than 15 percent.

Furthermore, the optimal pore size also depends on the size ratio x. We discuss this behavior and physical as well as economical limits of this optimization. Finally, our findings can easily be mapped onto the inverse cycle, a blue engine, which allows a maximization of the harvested blue energy.

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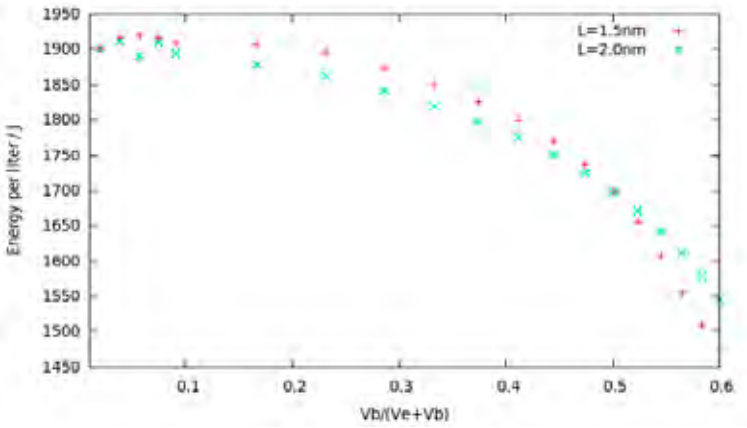

Figure: Required energy for the desalination of one liter of sea water, shown against the ratio x=Vb/(Ve+Vb) for fixed pore sizes L.

Membrane Capacitive Deionization: definitions and double layer modeling

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Membrane Capacitive Deionization (MCDI) employs ion-exchange membranes together with porous carbon electrodes to desalinate water. In MCDI ions are stored both in the interparticle pore space between carbon particles, as well as within the electrical double layers (EDL) formed inside the carbon micropores. In the micropore EDLs, electronic charge in the carbon is exactly matched by the ionic charge in the water-filled micropores (diffuse or Donnan layer), see Fig. 1. The main advantage of MCDI is that the charge efficiency is much higher than in CDI, at low enough salt concentration approaching unity. This leads to a reduction in energy consumption. Also, in MCDI a reversal of the voltage is possible during discharge (regeneration), which helps to speed up ion release. In CDI, voltage reversal lead to a frequency doubling of the CDI cycles. Finally, in MCDI it works better than in CDI to operate in constant-current mode, leading to a stable effluent salt concentration at a level that can be tuned by modifying the current.

In the presentation we discuss different meanings of terminology used in the CDI-field for efficiency: charge efficiency, current efficiency, Coulombic efficiency, and salt removal efficiency. We compare electrostatic double layer models that can be used to describe ion adsorption and charge (Gouy-Chapman-Stern versus modified-Donnan model). Finally, we describe how these microscopic EDL-models can be included in a two-dimensional electrode transport model.

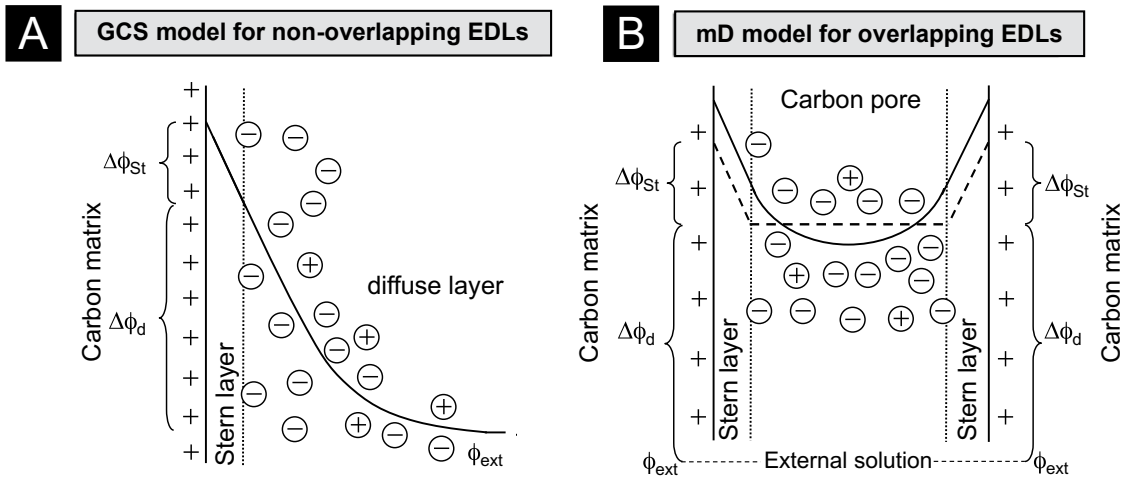

Fig. 1. Classical Gouy-Chapman-Stern EDL model vs modified-Donnan model for carbon micropores.

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Multiphysics simulation of Membrane Capacitive Deionization for mixed streams

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Membrane capacitive deionization (MCDI) has emerged over the past years as an energy- and cost-efficient technology for desalination of waters with low to moderate salt content in applications such as domestic water softening or desalination of cooling tower make-up water [1]. With the aim of broadening the range of applications of this technology, we have been investigating the possibility of MCDI treatment for more 'complex' wastewaters and industrial process streams - such as biomass hydrolysates [2] - which contain both salts and organic compounds. This combination tends to be problematic for conventional separation processes; therefore there is a need for new techniques for efficient recovery of the target compounds and/or water. The low fouling susceptibility and high energy efficiency of MCDI make it a potential alternative separation technology for such types of streams. Initial tests indicated that the current commercial MCDI setups do not always operate optimally in the presence of organic compounds. Therefore a better understanding of the behavior of different types of organics within MCDI, and of the key factors determining overall performance on mixed streams is needed, in order to develop tailored designs and operational modes.

In the coming future, the goal of this research is to develop a COMSOL multiphysics FEM model to develop insight into the transport processes occurring in MCDI applied to mixed streams, and subsequently use this model as a design aid for novel applications.

Points of attention are CFD-based geometry optimizations to minimize dispersion (in order to e.g. enhance product recovery), strategies for mitigating concentration polarization effects on both the spacer and electrode side of the membrane, prevention of faradaic reactions, fouling, scaling and clogging, and selection of ion exchange membranes with an optimal balance between mobility of organics and electrical resistance.

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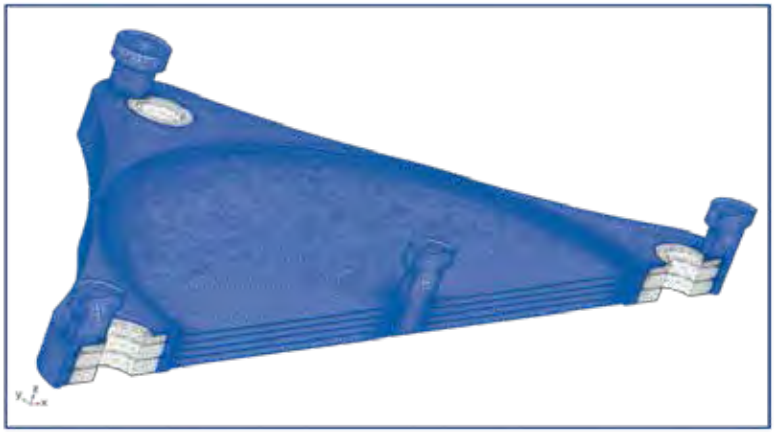

FEM geometry of an experimental CDI cell

Keynote

Flow-through electrode capacitive desalination and experimental characterization of desalination electrodes

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Capacitive deionization (CDI) is a novel approach to water desalination which is attracting significant and growing research attention [1,2]. A CDI cell typically consists of two porous carbon electrodes between which feedwater flows through an open channel or porous dielectric separator [3]. Charging the electrode pair to a voltage difference of approximately 1 V causes salt ions in the feedwater to transport to, and be electrostatically held against, oppositely charged carbon surfaces. In this lecture, I will describe the development of what we termed "flow-through electrode capacitive desalination" [4]. In this system, the feedwater flows directly through the porous electrodes themselves rather than between the electrodes. While flow-through electrodes for desalination were first proposed in the 1970's [5], the systems developed at that time suffered from electrode degradation and limited performance. Now, 4 decades later, we have developed a novel, high performance flow-through electrode capacitive desalination system utilizing newly developed hierarchical carbon aerogel monolith electrodes. The pore structure of this electrode material is designed to allow for simultaneously high salt sorption and efficient fluid flow-through. I will describe the physical principles and prototype results demonstrating that flowing through (rather than between) the electrodes enables significant advantages in both desalination time and feed concentration reductions.

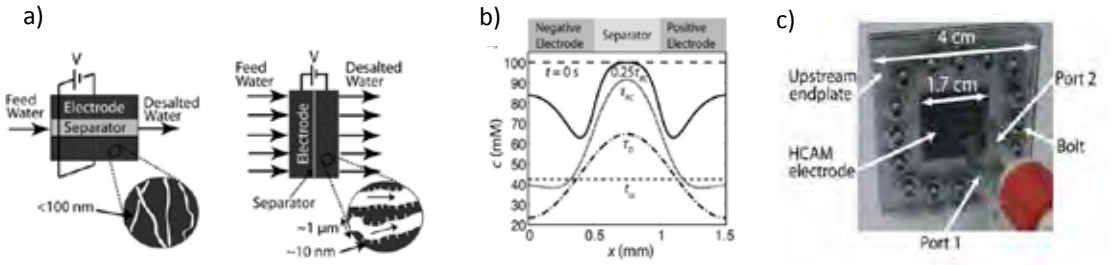

Figure 1: a) Schematic of the concept of flow through electrode capacitive desalination versus typical flow between CDI cells. b) Porous electrode transport model results demonstrating the evolution of salt concentration in a complete and charging CDI cell. c) A picture of our fabricated flow through electrode capacitive desalination prototype.

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In the second part of the lecture, I will discuss our recently developed experimental techniques to characterize and study CDI cell and porous electrode performance. Characterization of CDI systems typically involves measurements of the downstream (treated) water conductivity [1,2,3]. However, the conductivity data obtained can often be dependent on a large number of system and flow parameters, and is not well suited to detect effects such as variations in sorption performance between electrodes. We have developed several unique tools which allow for improved and more insightful studies of CDI systems, and thus can be used to catalyze future performance improvements. These include a first time measurement of spatially resolved chloride salt concentration between charging electrodes in a CDI cell (using fluorescent microscopy), and a framework for electrochemical impedance spectroscopy (EIS) studies of multiscale porous electrodes [6,7]

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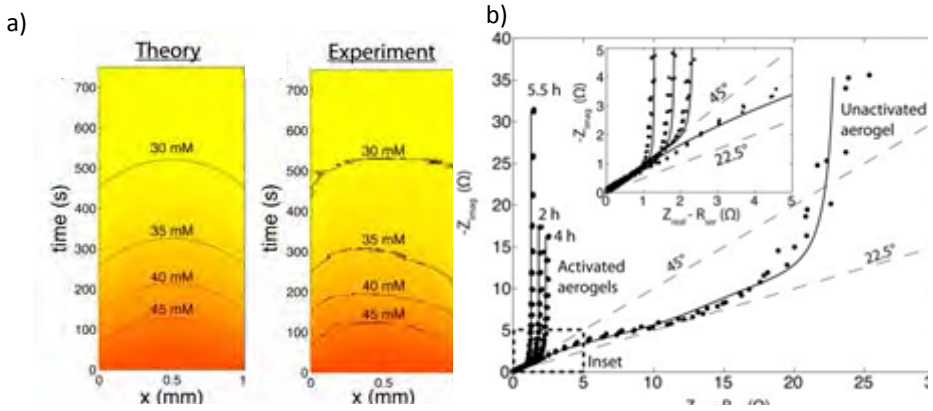

Figure 2: a) Theoretical predications and direct measurements of spatially resolved salt concentration between charging porous electrodes of a CDI cell. b) Circuit model predictions (black lines) and measurements (black dots) of the impedance of porous electrodes with multi-scale pore structures for CDI.

Enhanced energy efficiency in increased discharging voltage Capacitive Deionization

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Capacitive deionization (CDI) is an electrochemical method for water desalination employing porous carbon electrodes. In the porous carbon electrodes, electrical double layers are formed, which consist of two phases: the electron conductive matrix, in which electrons are stored, and the diffuse layer, in which ions are stored to compensate the electrical charge. During the adsorption phase, electrons are transported from the negatively polarized electrode towards the positively polarized electrode. To keep the electrodes electroneutral, for every electron transported, a counterion is adsorbed into the diffuse layer or a co-ion is desorbed from the diffuse layer, see Fig. 1. The desorption of these co-ions results in a charge efficiency, that is the ratio of salt adsorbed over the electrons transported from the positively polarized to the negatively polarized electrode, below unity. A charge efficiency below unity results in higher energy demands, because more electrons are transported per salt molecule removed from the brackish water, and is therefore disadvantageous.

We show how the charge efficiency can be increased by increasing the discharging voltage, such that we can avoid the adsorption of co-ions in the porous carbon electrodes during the desorption phase. Consequently, these ions cannot be desorbed during the adsorption phase either.

We conducted experiments employing electrodes made of commercially available microporous activated carbon. We applied a constant charging voltage of 1.2 V during the adsorption phase and different constant discharging voltages from 0 V up to 0.9 V during the desorption phase. Our experiments were conducted in flow-by mode, that is, the water flows through a spacer channel in between the two oppositely polarized electrodes. The adsorption and desorption time of all the experiments was 1200 s, so that, at the end of each adsorption and desorption phase, there was no net transport of electrons and ions to and from the electrodes. We cycled three times through the adsorption and desorption phase before actually collecting the data, so the salt adsorption and the charge density did not differ between one and the other cycle. The experiments were performed with three different inflow concentrations of NaCl: 5, 20 and 80 mM. We compared the experimental data of the salt adsorption and the charge density with theoretical calculations using the modified Donnan model [1].

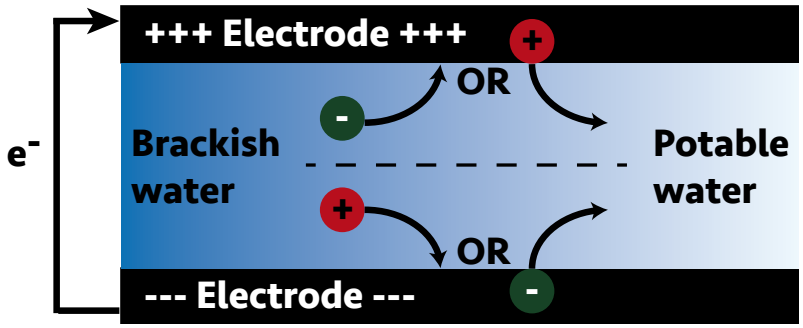

Figure 1 CDI cell during the adsorption phase. Every electron transported from the negatively polarized electrode to the positively polarized electrode results in the adsorption of a counterion into or the desorption of a co-ion from both oppositely polarized porous carbon electrodes.

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Seawater Desalination and Energy Recovery using Flow-electrode Capacitive Deionization (FCDi)

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The energy-efficient capacitive deionization (CDI) techniques have been used for desalination of low salt concentration water below brackish water and are not utilized for the seawater desalination, because it has a limited ion adsorption capacity of the fixed porous carbon electrode. To overcome the limitation of current CDI systems, we designed flow-electrode capacitive deionization (FCDi) system that uses flow-electrode. The flow-electrode, which is comprised of carbon suspension of activated carbon and 0.1 M NaCl solution, flows through a flow-path carved on the current collector instead of the fixed carbon electrode of the conventional CDI. FCDi unit cell exhibited continuous desalting performance more than 95 % of removal efficiency with respect to not only 32.1 g L^{-1} of NaCl solution but also 2.0 g L-1 of concentration. This result demonstrates that the flow-electrodes, fed in the FCDi cell, have infinite ion adsorption capacity and allow continuous seawater desalination. Also, we observed that energy supplied during charge step can be recovered by constant current discharge of flow-electrode, which is fully charged at various voltages.

Ultrasound-assisted Preparation of Electrospun Carbon Nanofiber/graphene Composite electrode for Capacitive Deionization

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The capacitive deionization technology (CDI) has drawn much attention because of its potential as an energy-efficient alternative for producing fresh water from salted water sources. For the CDI technology, the electrode materials with tuned pore structure and functionality such as conductivity are the key to the efficient desalination process. In this talk, we report on the design and fabrication of electrospun carbon nanofiber/graphene (CNF/G) electrodes by electrospinning polymer nanofibers, in which graphene oxide was sprayed simultaneously, and the composites were heat-treated. The freestanding carbon nanofiber web acts as a framework for sustaining graphene, and helps to prevent the agglomeration of graphene, while the graphene helps to improve the conductivity of the as-obtained CNF/G composites that exhibit an electrosorption capacity for NaCl of 15 mg/g, which is about 2.5 times of the adsorbed amount in the case of the pristine CNF without graphene. This has demonstrated that the graphene is indispensible for making high perforamnce CDI electrodes with desired structure and capacity.

Keywords: Carbon fiber, Electrospinning, Graphene, Capacitive deionization

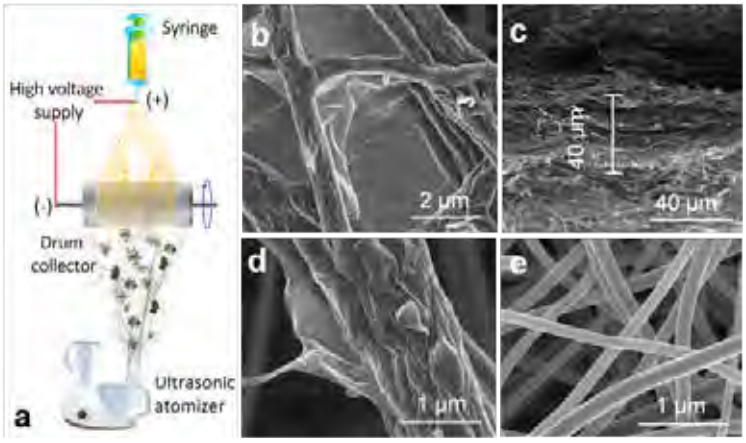

Figure 1 (a) Schematic of the electrospinning coupled with ultrasonic spray process, (b) top-view and (c) side-view SEM images of the as-prepared CNF/G, (d) SEM image of the individual CNF/G fiber at higher magnification, and (e) SEM image of the pristine CNF.

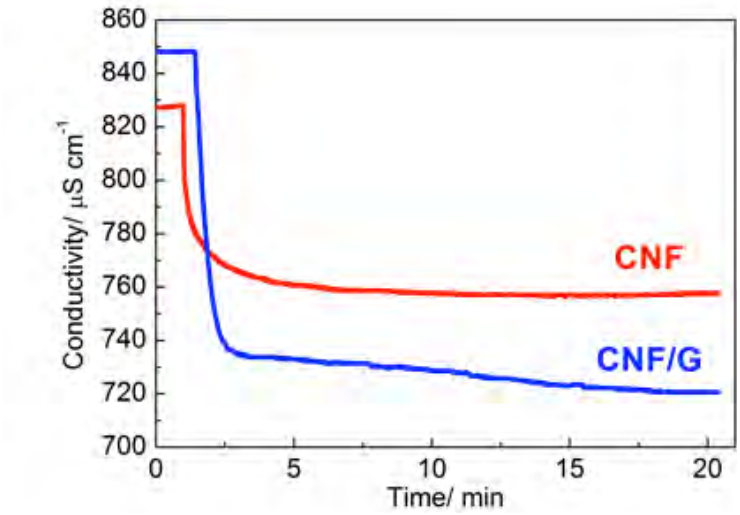

Figure 2 Desalination curves of CNF and CNF/G electrodes as a function of time in CDI, for which the test conditions are: the cell voltage, 1.2 V; the flow rate of water, 15 mL/min.

Capacitive deionization (CDI) of NaCl solution using activated carbon electrodes in a novel CDI module

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A novel CDI module is introduced using activated carbons as electrode in capacitive deionization process. Voltage is not applied to each electrode as in the common CDI module but rather on the metal plate outside the entire module. The **effects of voltage and electrode pair number on the performance of the novel CDI module are** investigated, and the **novel CDI module is compared with the common CDI module.** The experimental results show the novel CDI module exhibits higher electrosorption capacity, shorter desorption time, and lower energy consumption than those of common CDI module.

Keyword: Capacitive deionization, electrosorption, module

Keynote

Salt removal, water recovery and energy consumption in Membrane Capacitive Deionization

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Membrane Capacitive Deionization (MCDI) is an emerging new electrochemical desalination technology, which is suitable for the removal of ions from brackish water up to concentrations of about 100 mM (ca. 5000 ppm). In MCDI ions are removed from feed water by applying an electrical potential difference between two electrodes, whereby an ion-exchange membrane is positioned in front of each electrode. Water can flow in the spacer compartment, which is situated between the oppositely charged electrodes. Ions that are removed from the feed water are temporarily stored in the electrical double layers that are formed at the electrode-water interface. In MCDI, the co-ions that are expelled from the electrical double layers cannot enter the flow channel because they are blocked by the anion and cation exchange membranes. These co-ions are therefore retained in the interparticle space in the electrode compartment. Because of charge neutrality these co-ions need to be compensation for by counterions, which pass the ion exchange membrane from the spacer compartment. In MCDI, the expelled co-ions therefore lead to an increase of the total ion storage capacity of the electrodes.

The electrodes need to be regenerated once they are saturated with ions, which can be done by reducing or even reversing the applied voltage. In MCDI, the released counterions cannot migrate to the opposite electrode, because of the presence of the ion exchange membranes. Therefore, during electrode regeneration high concentrations of salt ions can be obtained in the flow compartment, which can subsequently be flushed out with a small amount of water, resulting in high water recoveries.

Dividing a feed-water stream into a dilute stream and a stream concentrated in ions costs energy and for any desalination technology the energy consumption is a significant part of the Total Cost of Ownership. In MCDI, the electronic charge is fully charge balanced by counterion adsorption and the charge efficiency, which is the ratio of the ionic charge over the electrical charge, is therefore (close to) unity. As a consequence the energy use is directly proportional to the amount of ions that are being removed from the feed water.

In this paper we discuss experimental results of a MCDI operation which shows how MCDI is ideally suited to achieve both high ion removal efficiency and high water recovery, which makes this an attractive technology for many applications. Furthermore, we also present data for the energy consumption at different salt concentrations and salt removal levels. We demonstrate that up to 83% of the energy used for charging the electrodes during desalination can be recovered in the electrode regeneration step. This can be achieved by charging and discharging the electrodes in a controlled manner by using constant current conditions. By implementing energy recovery as an integral part of the MCDI operation, the overall energy consumption can be as low as 0.26 $(kW \cdot h)/m^3$ of produced water to reduce the salinity by 10 mM. In comparison, by using reverse osmosis under similar conditions the energy consumption is about 1kWh per m^3 of produced freshwater. This means that MCDI is more energy efficient for treatment of brackish water than reverse osmosis.

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Development of Functionalized Graphene Electrode for Water Softening

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The hardness in water represents the contents of divalent ions such as iron, manganese, copper especially, magnesium and calcium. Conventional softening technologies including reverse osmosis (RO) and electrodialysis (ED) for hardness treatment have been developed. However, they still have several disadvantages such as fouling of membrane and high operating cost. Of late, Capacitive Deionization (CDI) is attractive technology for water desalination and softening by very low capacitive current of electrochemical double layer. Among various carbon-based materials used for electrode fabrication, graphene (rGO) has been intensively studied due to its excellent electrical conductivity and high surface area. However, graphene difficultly disperses in water because of its strong Van-der-Vaals force and hydrophobicity, as well as low capacitance causing limitation in making CDI electrode. In this work, we successfully prepared uniformly-dispersed rGO in aqueous solution through control reduction process of graphite oxide and hence enhance ion adsorption ability of in CDI cell system. Additionally, graphene also is composited and activated by MnO_2 in Alkaline condition at high temperature hence, enhance considerable surface area, specific capacitance by MnO_2 presentation as well as improve CDI performance. The effect of parameters to CDI process is investigated in order to optimize the softening efficiency. The voltage of 1.5 V is chose to supply power for this system and maximum ion removals gained can be comparable to other researches.

Keywords: Capacitive Deionization, Graphene, MnO2, Applied voltage, Flow rate.

Enhanced energy generation with capacitive electrodes driven by Exoelectrogen-generated ionic currents

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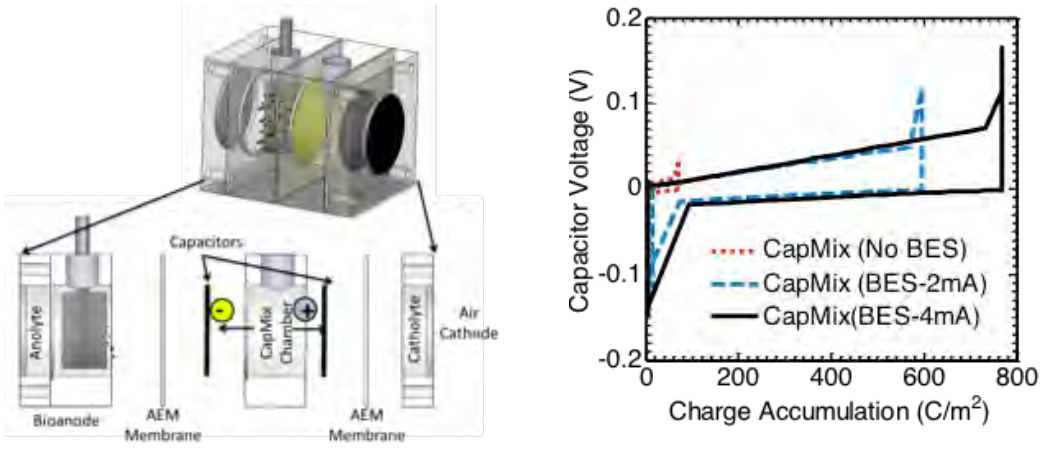
Bioelectrochemical systems (BESs) have the potential to generate electricity through coupling wastewater organics oxidation by bacteria, to a cathodic reaction such as oxygen reduction. Power production from BESs has improved over the last decade, yet still remains on the order of 1-2 W m^{-2} (cathode). The recent synergy between salinity gradient energy technologies (e.g. reverse electrodialysis (RED)) and microbial fuel cells was shown to significantly boost the power from BESs by nearly 5 times [1, 2]. Yet RED currently requires a large number of ion exchange membranes, which results in high cost.

Capacitive mixing (CapMix) is an emerging salinity gradient energy technology which harvests energy through the controlled transfer of ions to and from capacitive electrodes in river and seawater solutions [3, 4]. CapMix has suffered from low power densities, but is still promising because materials cost are low. Experiments were conducted to evaluate the potential synergy between BESs and CapMix (Fig 1a). Results indicated that the presence of the BES electric field improved the charging rate of the capacitive electrodes. This resulted in an increase in the energy harvested from the CapMix process with synthetic river and seawater solutions by 60 times from 0.04±0.003 mJ $cycle^{-1}$ (without BES) to 2.64±0.240 mJ $cycle^{-1}$ (with BES)[5] (Fig 1b). Furthermore, the electric field induced charging mechanism, may have implications for enhancing desalination rates in membrane based capacitive deionization systems.



a) b)

Figure 1 (a) Capacitive mixing – Bioelectrochemical system schematic and (b) energy extracted from the combined systems as a result of different BES operating conditions.

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Solid-State NMR Studies on Adsorption of Electrolyte Ions in Carbon Materials with well-defined Porosity

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The demand for renewable energy sources and advanced energy storage devices steadily increase in this century of dwindling fossil fuel resources. Among them, electrochemical double-layer capacitors (EDLCs) stand out due to their high power densities and nearly unlimited cycle life [1]. Due to their chemical inertness, high electric conductivity, and large specific surface area, porous carbon materials are used in most EDLCs. Further tuning of their structure and a better understanding of the relationship between their properties and the EDLC performance is highly desired. Recently, Chmiola *et al.* found that there is a capacitance increase when the pore size of the carbon materials becomes lower than the critical solvent shell size and the formation of a double-layer would not be possible from the theoretical point of view [2]. These findings forced the development of novel microporous carbon materials for the use in EDLCs as well as the use of new techniques for the characterization of the carbon-electrolyte interaction. Next to small-angle neutron scattering and theoretical simulations especially nuclear magnetic resonance spectroscopy (NMR) was found to be a useful method for the investigation of the ion adsorption in microporous carbons [3-4].

In the present contribution a series of porous carbon with well-defined pore sizes ranging from 0.6 nm to 4.5 nm is used for solid-state NMR investigations on the adsorption of Tetraethylammonium-tetrafluoroborate ($TEABF_4$) ions (1M solution in acetonitrile). Our investigations focus on ordered mesoporous carbide-derived carbons (OM-CDCs), mesoporous CMK-3, and microporous CDCs. Materials are loaded with the electrolyte solution or the pure solvent for comparison. Magic angle spinning (MAS) ^{1}H, ^{11}B, and ^{13}C NMR measurements show that the chemical shift of NMR active nuclei located at molecules adsorbed in porous carbon materials of comparable degree of sp^2 hybridization is strongly correlated with the pore size [5]. However, the characteristic diamagnetic shift is clearly influenced by the hybridization state of the carbon atoms. In carbon materials with sufficiently large pores, electrolyte molecules tend to reside closer to the pore walls than the solvent molecules (AN) which are to some extent “screened” from the influence of the pore walls by the electrolyte. Removal of the solvent by evacuation results in a removal of the solvent shell and brings the electrolyte molecules into closer contact with the pore wall. If adsorbed in pores <1 nm diameter, solvent removal does not result in a further increase of the diamagnetic shift. This supports the idea that the electrolyte molecules do not exhibit an intact solvent shell in such small pores.

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Temperature and size effects on the desalination of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigate the effect, which either varying the temperature or the pore and engine sizes have on the properties of blue engine and desalination cycles. Desalination cycles were found to be most effective when a huge bath of cold water is used. There is a ~10% decrease in required energy when changing from equatorial to arctic sea water and another ~10% decrease when changing the volume of the desalination bath from the volume of the engine to a 10x larger one.

Furthermore, we studied the effect of using water at different temperatures and electrodes build from pores of different sizes within one cycle. Saline water reservoirs at different temperatures can be obtained by e.g. pumping sea water from depths to the surface or by using cooling water from industrial facilities in an intelligent way. Desalination becomes increasingly cheap when performing the charging step in sea water of lower temperature than the discharging step. Interestingly, the characteristics of the engine (pore size, pore volume, bath volume) can be tailored such that the required energy vanishes already for small temperature differences.

These positive temperature and size effects on the efficiency are not at all exclusive to desalination cycles; similar effects are also observed in blue energy cycles. We find that blue energy harvesting can be enhanced when fresh water is used which has a higher temperature than the sea water. For large temperature differences of the order of 50 degrees this boosts the work per cycle by a factor of two, compared to existing techniques (see figure).

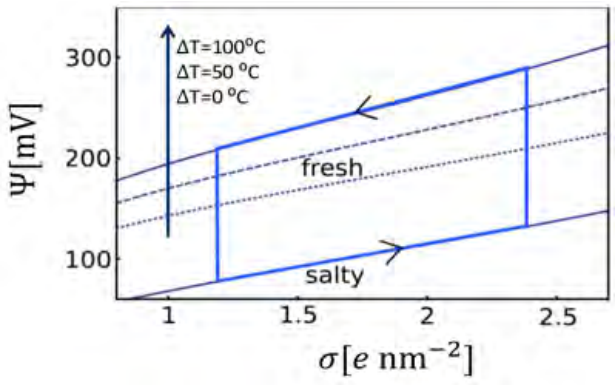

Figure Blue energy cycle in the potential – charge representation. Stroked lines represent the upper part of the cycle, connected to fresh water reservoirs of different temperature.

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Preparation of Chestnut-like Carbon Electrodes for Capacitive Deionization

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Recently, the reliable supply of clean fresh water is becoming increasingly difficult as global and regional development accelerates, and this has become a bottleneck issue for the sustainable development of many countries. Chestnut-like carbon were prepared PCNFs grown on activated carbons using the catalytic gasification with Fe - Ni catalysts in air. Catalytic gasification of activated carbon was carried out at 400 for 1 h at each temperature. The PCNFs grown on activated carbon at 600 °C using activated carbon gasified with a 0.1% Ni-Fe catalyst at 450 °C. The surface area of Chestnut-like carbons were 2401 m2/g. Additional specific capacitances of Chestnut-like carbon are significantly higher than those of other activated carbons. Chestnut-like carbon electrodes show approximately 44% retention of the specific capacitance, which is higher than that of the virginity activated carbon. Thus, Chestnut-like carbon electrode can be predicted to yield better performance in the capacitive deionization (CDI) process.

Multidisciplinary modelling of CDI using optimisation tools: implications for agricultural applications

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Capacitive deionization is a viable method of water treatment in an increasing number of small scale and niche applications but is less cost effective at higher volume applications above the megalitre per day range. As the per-gram cost of adsorbent materials decreases with advancements in manufacturing and design, CDI could become the answer to significant environmental challenges of larger scale. The work presented here addresses the issue of scale up with particular attention given to the accuracy of process costing and optimisation. Models of the physical aspects of CDI developed by Biesheuvel et al (2009[1], 2011[2]) are used as the basis of the modelling undertaken here with the optimisation tool AspenTech used to obtain a more accurate estimate of process level performance as a function of key design and process variables. In particular, consideration is given to possible CDI configurations within a conceptualised large scale process and the Aspen modelling package used to examine impact of process variables on cost effectiveness. The implementation of CDI in the simulation environment is undertaken via a custom module utilising a discretised form of the available physical models of the CDI process. The optimisation package developed enables rapid identification of suitable applications in situations where reverse osmosis has shown to be non-viable. In this analysis we focus on treatment of brackish water for use in agriculture/horticulture with particular attention given to the impacts of water demand and brackish water quality on optimal choice of process parameters and viability of the proposed technology. Further development of this modelling framework could provide the impetus to attract the resources needed to further accelerate the cost reduction process.

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Water Denitrification using Energy-Efficient Capacitive Deionization Technology

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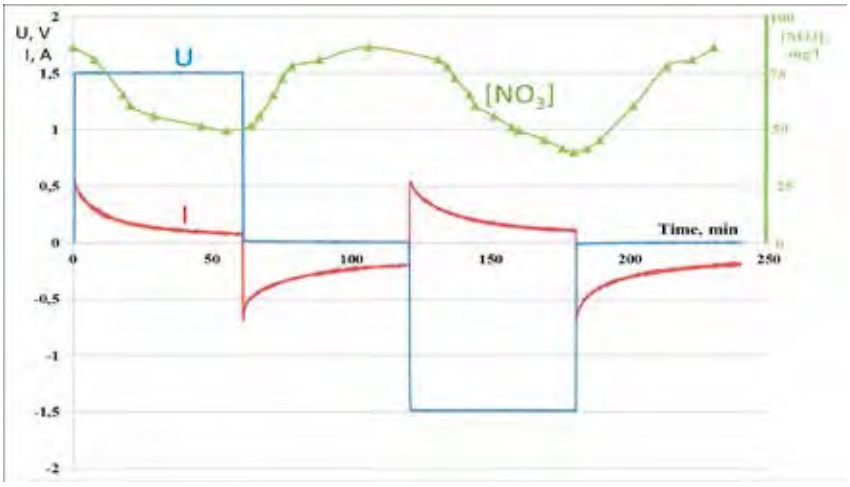
Recent water quality monitoring has shown the ingress of nitrates into the groundwater. The over-application of fertilizers results in the increased nitrate level and the exceeding maximum permissible concentration (MPC) for nitrates in many areas around the world that is a big risk for human health. Therefore, the importance of creation and development of water denitrification technologies grows year after year.

The results of the investigation on nitrate sorption in the CDI units are presented in the paper. The electrodes for the CDI units were manufactured from carbon material SAUT-1C which was modified by titanium. Deposition of titanium coating was made using the Arc-PVD method. Weighted samples of pure chemicals as well as distilled water were used for preparation of standard aqueous solution. The solution was circulated in a circle. The total volume of the solution was 4,7 L, and the circulation flow rate of the solution was 1 L/min. The ion concentration was measured using the potentiometric method, and the total salt content was controlled using the conductometric method. The measurements were made in a buffer volume. The programmable low-voltage power supply unit CDS1-5M10 was used to supply the electrochemical module with power. The power supply unit includes five separate modules with each having the operating voltage range of -1,5 V ÷ +1,5 V as well as the operating current range of 0-10 A.

The typical current and voltage oscillograms of the CDI units within the charging-discharging cycles as well as the variation in nitrate concentration level of the treated solution are shown in the figure. The decrease of the nitrate concentration by several times (2-5) to the level below the MPC for nitrates (45 mg/l) was demonstrated. The adsorption of sodium, potassium, calcium ions and chlorides was also studied. It was shown that the ion adsorption is inversely proportional to the ion valency in aqueous solution. Thus, for the same total transferred charge the number of calcium ions being adsorbed on the electrode surface is twice less than the number of monovalent sodium ions that corresponds to the ion valency. It was also shown that the specific adsorption ability of the carbon material SAUT-1S modified by titanium for sodium chloride solution (5000 ppm) is 15,3 mg per 1 g of carbon material.

Therefore, it was shown that the CDI technology can be applied for water denitrification as an energy-efficient method.



Posters

Fabrication of composite capacitive deionization electrodes using biochar materials and conductive membranes

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Capacitive deionization (CDI) is considered as a promising and sustainable technique for energy storage and brackish water desalination. However, the material selection and fabrication of low cost electrodes is one of the main limiting factors for large-scale commercial applicaiton of CDI technology. In this study, composites of low-cost and renewable biochar, produced from woody biomass and a conductive polymer, PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) are evaluated as CDI electrodes. PEDOT:PSS is a promising candidate to improve the intra-particle conductivity and ion adsorption capacity of the electrode system due to its high conductivity, processibility, effective binding material, and environmental stability, and low cost. The compatibility of PEDOT:PSS with mesoporous carbon shows applicable potential to apply the PEDOT:PSS/tailed-carbon system in CDI chambers. The salt adsorption/desorption efficiency is measured in constant potential and cyclic voltammetry experiment and the electrochemical property of the electrode is studied by using impedance spectroscopy. The performance of fabricated electrodes will be compared to biochar capacitive electrodes fabricated with a conventional binding agent (i.e. PVDF).

Keywords: Capacitive deionization, Biochar supercapacitor, Conductive polymers, CDI flow design.

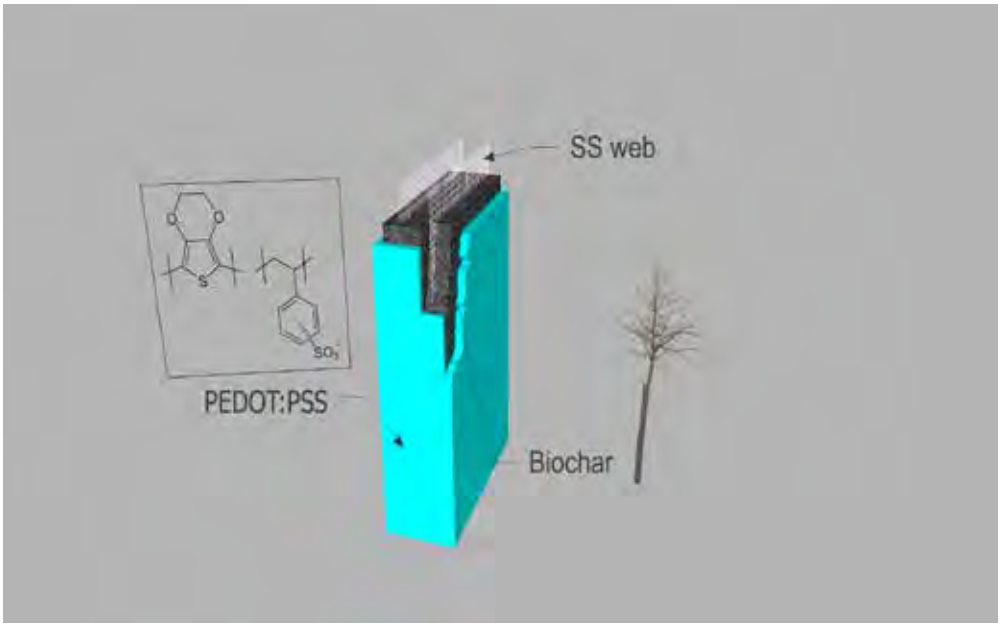

Figure CDI electrode constructed with biochar, stainless steel web, and PEDOT:PSS conductive polymer.

Posters

Electrokinetic remediation of fine clay soils contaminated by Hydrophobic organic pollutants

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Active accumulation of hydrophobic organic compounds in the environment sets the task of the development of effective methods directed to their removal from water, sludge and soils. The most problematic objects for decontamination are dispersions, which contain fine clay components. First of all, due to peculiar surface and volume properties and large specific surface area of this type of dispersions, they are the most inclined to retain pollution. Secondly, due to the high values of hydrodynamic and aerodynamic resistances, the choice of effective decontamination method is extremely limited.

Electrokinetic treatment is the method for which the fine clay soil specific properties ensure its effectiveness in removing of uncharged organic compounds. For the effective management of the process it is necessary to provide a stable electroosmotic flow and to reach water-solubility of hydrophobic contaminants.

The rate of electroosmotic transport depends on the zeta potential of soil particles, which in turn depends on the pH of a pore solution. Thus, the important aspect of soil decontamination is regulation of pH. Electrohydrodynamic method of regulation of pH and intensification of electroosmotic permeability for enhancing the efficiency of the removal of hydrophobic organic compounds is proposed and theoretically and experimentally substantiated.

Another aspect is the correct choice of surfactants, which provide desorption and movement of hydrophobic contaminants into the pore solution. Cationic surfactants can not be used since clay soils have a negative electrokinetic potential, which decreases upon introduction of positively charged surfactants leading to a diminution of the electroosmotic velocity. Introduction of anionic surfactants increases the electrokinetic potential of soil particles accelerating electroosmosis, but in the same time these surfactants can charge the organic compounds leading to their electromigation in the direction opposite to electroosmotic flow, thereby also slowing down the rate of soil decontamination. Finally, nonionic surfactants do not charge the organic pollutants and therefore do not affect the velocity of electroosmosis. Thus, they are the most promising in soil remediation.

Studies of the effect of the type of surfactants on soil remediation efficiency were carried out on a model system, which is kaolinite contaminated by ortho-chlorotoluene (4.5 mg/g of kaolinite) using non-ionic surfactants (Triton X-100, Tergitol 5-S-7, Neonol AF-9-12) and anionogenic surfactant (sodium dodecyl sulfate).

The obtained experimental data demonstrated that the presence of anionic surfactant results in a significant increase of the velocity of electroosmosis in comparison with the velocity at the use of nonionic surfactants. For example, at the electrokinetic remediation with the use of sodium dodecyl sulfate 160 ml of electroosmotic liquid (10 volumes of pore solution) passed through the soil during 20 hours, while the introduction of a Triton X-100 increased the treatment time to 36 hours. However, as expected, anionogenic surfactant significantly reduced decontamination efficiency - 70.7% of residual ortho-chlorotoluene compared to 26.0% in the case of non-ionic one that is caused by appearance of their own electromigration mobility

The velocities of electroosmosis for different nonionic surfactants are almost the same, but the degree of pollutant removal is much different. Tergitol 5-S-7 provided decontamination almost at the same level as it was obtained at presence of Triton X-100 (27.7% of the residual ortho-chlorotoluene). The best results were obtained for Neonol AF-9-12 (at the passage of 160 ml of electroosmotic liquid the residual ortho-chlorotoluene decreased to 5.7%). The increase of the treatment time allows to decrease the residual ortho-chlorotoluene to the rather small values, however this is accompanied with increase of power consumption.

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