Addressing the Water-Energy Nexus with Electrochemistry

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Motivation and Overview

Increased urbanization, climate change, and population growth, together with expansion of agriculture, and a dramatic increase in oil and gas production, have resulted in soaring water use. The infrastructure for municipal drinking water and wastewater treatment in many cities is failing and in need of major renovations. In addition, large volumes of industrial wastewater are contaminated with high concentrations of salts, toxic heavy metals, and organics. These activities are met with challenges associated with both water quality and quantity, and severely impact the energy efficient management of our nation's water resources. For example, centralized water treatment has low energy efficiency and the resources for efficient treatment are not readily available in remote areas. In addition, the treatment of multi-contaminant waste streams requires complex and energy intensive treatment trains. There is a need for both technological and scientific innovation to address the challenges posed by this 'water-energy nexus'.

Electrochemical-based water treatment technologies have emerged as potentially transformative solutions to meeting these challenges. Electrochemical reactions can produce oxidants, reductants, acids, bases, and coagulants on-site, which eliminates the need for shipping and storing large volumes of corrosive or potentially dangerous chemicals, and thus allows for decentralized and remote water treatment. Electrochemical desalination and electrocoagulation technologies can achieve higher performance with less energy than traditional processes by reducing intensive pre-treatment expenditures and chemical inputs, thereby reducing the cost and increasing their viability for oil and gas water treatment. Additionally, electrochemical technologies can easily be coupled to renewable energy sources and incorporate energy recovery strategies that further reduce their fossil fuel dependence.

We have an institutional-wide commitment to electrochemistry at UIC, which is evident in faculty research, facilities, and education, and the UIC Electrochemistry Collaborative (https://energyinitiative.uic.edu/energy/uic-electrochemistry-collaborative) provides one such community for cross-disciplinary dialogue on electrochemistry. Researchers at UIC are actively involved in exploring both fundamental electrochemical and ionic processes that are relevant to water treatment and developing novel electrochemical water treatment technologies. Examples of fundamental work include 1) studies of electric field-induced ion distributions at aqueous interfaces, 2) mechanisms of ion transfer across liquid interfaces, 3) influence of charge on self-assembly and dynamics (of surfactant, proteins, particles and polymers), and 4) advanced imaging of contaminants at electrode/solution interfaces. Examples of technological innovations include 1) reactive electrochemical membranes that eliminate membrane fouling and remove multiple classes of water contaminants, 2) the use of electrical fields for the synthesis of nanotube membranes, 3) the coupling of electrochemical water treatment with electrochemical CO_2 reduction to useful fuel products, 4) development of electrochemical desalination and electrocoagulation for oil and gas water treatment, and 5) electrochemical sensing of trace-level contaminants in various aqueous streams. We offer multiple academic courses focused on electrochemical methods and processes, ionic transport, and thermodynamics, which are necessary to design and advance electrochemical treatment processes. We have generated $3.5M in external funding and published 47 peer-reviewed manuscripts focused on electrochemical related water research. We have trained a diverse group of graduate and undergraduate students and disseminated our key results to experts in various specialized fields, industrial stakeholders, and the general public. Below we highlight representative research, facilities, and education at UIC utilizing electrochemical processes for water treatment.

Representative Research

UIC is active in developing electrochemical technologies for water treatment and understanding the fundamental science enabling these technologies. As a result, collaborations have been developed between faculty in the basic sciences (Chemistry, Physics) and core engineering departments (Chemical Eng. (CHE), Mechanical and Industrial Eng. (MIE), Materials and Civil Eng. (MCE)). These collaborations are detailed below.

Reactive Electrochemical Membranes. Work in Prof. Brian P. Chaplin's group has resulted in the development of a class of patent pending ultrafiltration reactive electrochemical membranes (REMs).[1-3] The REMs are comprised of conductive Ti_nO_{2n-1} ($4 \leq n \leq 10$) ceramic materials that are being studied for membrane fouling regeneration, compound oxidation/reduction, and disinfection of pathogens.[1-7] This work has been leveraged to initiate several collaborations at UIC focused on decentralized water treatment and energy recovery. For example, portable electrochemical disinfection units have been constructed and studied in collaboration with Prof. Karl Rockne (MCE),[6] and coupling contaminant oxidation with CO_2 reduction is being pursued in collaboration with Prof. Meenesh Singh (CHE) and Prof. Amin Salehi-Khojin (MIE). Collaborations are also underway on developing antifouling REMs for electrochemical desalination with Prof. Sangil Kim (CHE) and manufacturing hollow fiber REMs with Prof. Vivek Sharma (CHE). The longevity and phase stability of the REMs under anodic polarization is key to their long-term success, and is being investigated in collaboration with Prof. Jordi Cabana (Chemistry) using micro-X-ray diffraction.

Electrochemical Desalination and Electrocoagulation for Water Treatment. Effective treatment of produced water is essential for the sustainable operation of oil and gas industries. Such treatment involves removal of oil, grease, metal ions, organic compounds, and salt. Electrochemical technologies such as electrochemical desalination and coagulation can offer > 98% removal of salt and metal ions with a minimum energy consumption of 0.013 kWh per gallon of produced water. Electrochemical processes are suitable for water treatment due to 1) robustness to withstand moderate to harsh water conditions, 2) scalability to treat millions of gallons of water, and 3) flexibility to be integrated with the existing infrastructure for produced water treatment. Prof. Singh's group is developing efficient, robust, and scalable electrochemical desalinators and electrocoagulators for produced water, seawater, and wastewater treatment, which can be integrated with CO_2 reduction systems. Prof. Singh's group has identified design principles[8,9] and developed an efficient electrodialysis system that can produce concentration gradients in a photo/electrochemical device[10] operating in the near neutral-pH conditions (similar to the pH of produced water, seawater, and wastewater). Prof. Alan Zdunek (CHE) is also developing an electric-field enhanced ion-exchange water desalination process. A prototype has been developed consisting of a fluidized ion-exchange resin reactor coupled with an electric field that achieves efficient desalination. Prof. Zdunek is collaborating with Profs. Kim, Singh, and Chaplin to develop ion-exchange resins that are more suitable for high salt content removal and with cost-effective regeneration strategies. Such standalone solar-driven devices for desalination can be deployed in naval ships, remote locations where electricity is not accessible, oil wells, and residential units.

High Flux Nanocomposite Membranes. This project is focused on the development of nanotube-based composite membranes in which 1D tubes are aligned in a preferential direction with an electric field. 1D nanochannels enable extremely fast mass transport of water through nanometer-sized pores, rejecting particles both due to their size and charge. Prof. Sangil Kim (CHE) demonstrated that water flows 1000 times faster through nanotubes than through other pores of similar diameter.[11-13] The projects were supported by ARPA-E, DTRA, and DARPA, and two start-up companies (Porifera and NanOasis) were launched to commercialize nanotube-based composite membranes. Professor Kim received R&D 100 award in 2010 for the development of the nanocomposite membranes. At UIC, Prof. Kim has collaborative projects with Prof. Chaplin to investigate the ion transport mechanism in charged nanopores and with

Prof. Vikas Berry (CHE) and Prof. Vivek Sharma for the development of highly charged nanoporous membranes.

Fundamental Studies into the Science Underlying Water Treatment. Numerous opportunities exist for the investigation and application of the nanoscale behavior of water, and water-solute interactions, at a level to support innovation in the area of electrochemical-based water treatment technologies. These include, for example, the broad areas of particle-particle interactions and separations science and engineering.

Ionic interactions in water and at aqueous interfaces with, for example, water treatment membranes, underlie the effectiveness of many water treatment processes. Ongoing fundamental research in these areas at UIC includes work in Prof. Mark Schlossman's group (Physics) to understand interactions between ions in water and in organic solvents and in Prof. Vivek Sharma's group on interactions between charged polymers and charged surfactants.[14] Their work provides a nanoscale connection between the potential of mean force and ion distributions at interfaces.[15-18] Extension of this work to particle-particle interactions in collaboration with Prof. Robert Klie (Physics) and Prof. Petr Kral (Chemistry) could lead to increased efficiency in electrocoagulation and flocculation stages of industrial water treatment.

Schlossman's group is also investigating solvent extraction, in which target metal ions are selectively extracted from a complex aqueous mixture into an organic phase.[19,20] This process is used to separate toxic or radioactive metal ions from polluted water and nuclear waste, as well as to produce industrially relevant metals, including rare earth metals and base metals such as copper. The goal of ongoing studies is to understand the mechanism of solvent extraction on the nanoscale.

Nanoscale Imaging of Contaminants at Electrolyte/Electrode Interfaces. Mechanistic understanding of electrochemical processes is greatly enhanced by nanoscale imaging techniques. Prof. Shahbazian-Yassar's team (MIE) is equipped with microfluidic electrochemical devices that allow for nanoscale imaging of heavy metals interacting with nanoscale materials in aqueous solution using a high-resolution transmission electron microscope (TEM). Prof. Shahbazian-Yassar's group has been able to visualize electrochemical reactions at the surface of nanomaterials and the formation/dissolution of heavy-metal nanoparticles within liquid cells. These microfluidic devices are also compatible with X-ray elemental and chemical imaging techniques accessible at the Advanced Photon Source at Argonne National Laboratory. Prof. Jordi Cabana's group extensively uses these techniques and has frequent access to relevant instruments. Among others, X-ray fluorescence nanoimaging offers an extremely high sensitivity to several elements, with the possibility of probing their location in a solution, as well as their uptake by solids. Any redox changes involved in electrochemical processes of water treatment can be imaged by X-ray absorption spectromicroscopy. These tools are highly complementary to TEM, thus building a unique suite of imaging techniques.

Facilities

The research above is supported by state of the art facilities in individual researchers' laboratories, in the centralized *Research Resources Center* (RRC) at UIC (http://www.rrc.uic.edu), and in collaborative activities with nearby national laboratories. Additional core facilities are available for rapid prototyping at the Innovation Center (http://innovationcenter.uic.edu/wordpress/) and 3D printing at the Makerspace (https://engineering.uic.edu/makerspace/). Unique equipment include 1) state of the art scanning transmission electron microscope (JEOL-ARM200CF) with 0.08 nm resolution for surface imaging, 2) scanning electrochemical microscopy for studying the electrode/solution interface, 3) tensiometry techniques including pendant drop tensiometry, Langmuir tough tensiometry, and maximum bubble pressure tensiometer to elucidate the effect of charge on dynamics, interfacial properties, and adsorption kinetics, 4) electrochemical cell for studying ion transport through a single nanotube channel, 5) electrochemical microfluidic cells for nanoscale microscopy imaging, and 6) X-ray microdiffraction to probe activity and degradation in multifunctional structures. Our faculty are active users and administrators of specialized instrumentation at the Advanced Photon Source at Argonne National Laboratory. Therefore, the wealth of techniques available at these facilities is accessible to the team.

Education

UIC is a *Minority Serving Institution* and we have made a long-term investment in educating our diverse student population in the broad field of electrochemistry. Courses and seminars are offered in fundamentals of electrochemistry, electrochemical engineering, thermodynamics, interfacial phenomena, and electrolyte transport in the Chemistry and Chemical Engineering Departments. UIC also hosts Next Generation Electrochemistry (NGenE), a Summer Institute where a group of selected students explores the frontiers of electrochemistry under the guidance of leaders in electrochemical research in the nation. The Director is Prof. Jordi Cabana, from Chemistry. NGenE 2016 was funded by NSF, which subsequently requested a proposal, under evaluation, for the period from 2017 until 2019.

Future Outlook

The UIC Electrochemistry Collaborative has documented strengths in electrochemical science and engineering, materials development and characterization, and fundamental scientific understanding of ion transport at multiple interfaces that are relevant to understanding and advancing water treatment technologies. We are applying this expertise to develop new materials and processes to advance electrochemical water treatment technologies. Our goal is the development of next generation solutions that provide energy efficient drinking water and the efficient management of industrial wastewaters on the local and national scale.

UIC Electrochemistry Collaborative

The UIC Electrochemistry Collaborative (https://energyinitiative.uic.edu/energy/uic-electrochemistry-collaborative) is a group of UIC faculty whose interest in electrochemistry spans various disciplines. They focus on the next generation challenges in electrochemistry and bring to bear the latest advances in synthesis, nanoscience, dynamic and ultrafast measurements, *in situ* techniques, and theory and simulation to further advance electrochemistry.

References

(1) Zaky, A. M.; Chaplin, B. P., Porous Substoichiometric TiO_2 Anodes as Reactive Electrochemical Membranes for Water Treatment. *Environmental Science & Technology* **2013,** *47*, (12), 6554-6563.

(2) Zaky, A. M.; Chaplin, B. P., Mechanism of p-Substituted Phenol Oxidation at a Ti_4O_7 Reactive Electrochemical Membrane. *Environ. Sci. Technol.* **2014,** *48*, (10), 5857-5867.

(3) Guo, L.; Jing, Y.; Chaplin, B. P., Development and Characterization of Ultrafiltration TiO_2 Magneli Phase Reactive Electrochemical Membranes. *Environmental Science & Technology* **2016,** *50*, (3), 1428-1436.

(4) Jing, Y.; Chaplin, B. P., Electrochemical impedance spectroscopy study of membrane fouling characterization at a conductive sub-stoichiometric TiO_2 reactive electrochemical membrane: Transmission line model development. *Journal of Membrane Science* **2016,** *511*, 238-249.

(5) Jing, Y.; Guo, L.; Chaplin, B. P., Electrochemical impedance spectroscopy study of membrane fouling and electrochemical regeneration at a sub-stoichiometric TiO_2 reactive electrochemical membrane. *Journal of Membrane Science* **2016,** *510*, 510-523.

(6) Guo, L.; Ding, K.; Rockne, K.; Duran, M.; Chaplin, B. P., Bacteria inactivation at a sub-stoichiometric titanium dioxide reactive electrochemical membrane. *Journal of Hazardous Materials* **2016,** *319*, 137-146.

(7) Santos, M. C.; Elabd, Y. A.; Jing, Y.; Chaplin, B. P.; Fang, L., Highly porous Ti_4O_7 reactive electrochemical water filtration membranes fabricated via electrospinning/electrospraying. *Aiche Journal* **2016,** *62*, (2), 508-524.

(8) Singh, M. R.; Papadantonakis, K.; Xiang, C.; Lewis, N. S., An electrochemical engineering assessment of the operational conditions and constraints for solar-driven water-splitting systems at near-neutral pH. *Energy & Environmental Science* **2015,** *8*, (9), 2760-2767.

(9) Xiang, C.; Weber, A. Z.; Ardo, S.; Berger, A.; Chen, Y.; Coridan, R.; Fountaine, K. T.; Haussener, S.; Hu, S.; Liu, R., Modeling, Simulation, and Implementation of Solar‐Driven Water‐Splitting Devices. *Angewandte Chemie International Edition* **2016**.

(10) Jin, J.; Walczak, K.; Singh, M. R.; Karp, C.; Lewis, N. S.; Xiang, C., An experimental and modeling/simulation-based evaluation of the efficiency and operational performance characteristics of an integrated, membrane-free, neutral pH solar-driven water-splitting system. *Energy & Environmental Science* **2014,** *7*, (10), 3371-3380.

(11) Kim, S.; Jinschek, J. R.; Chen, H.; Sholl, D. S.; Marand, E., Scalable Fabrication of Carbon Nanotube/Polymer Nanocomposite Membranes for High Flux Gas Transport. *Nano Lett.* **2007,** *7*, (9), 2806-2811.

(12) Fornasiero, F.; Bin In, J.; Kim, S.; Park, H. G.; Wang, Y.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O., pH-Tunable Ion Selectivity in Carbon Nanotube Pores. *Langmuir* **2010,** *26*, (18), 14848-14853.

(13) Kim, S.; Fornasiero, F.; Park, H. G.; Bin In, J.; Meshot, E.; Giraldo, G.; Stadermann, M.; Fireman, M.; Shan, J.; Grigoropoulos, C. P.; Bakajin, O., Fabrication of flexible, aligned carbon nanotube/polymer composite membranes by in-situ polymerization. *Journal of Membrane Science* **2014,** *460*, 91-98.

(14) Zhang, Y.; Yilixiati, S.; Pearsall, C.; Sharma, V., *ACS Nano* **2016,** *10*, (4), 4678-4683

(15) Hou, B. L., N.; Yu, H.; Bu, W.; Chen, C.-H.; Yoon, J.; Lin, B.; Luo, G.; Vanysek, P.; Schlossman, M. L., Ion Distributions at the Water/1,2-Dichloroethane Interface: Potential of Mean Force Approach to Analyzing X-Ray Reflectivity and Interfacial Tension Measurements. *J. Phys. Chem. B* **2013,** *117*, 5365-5378.

(16) Laanait, N. M., M.; Hou, B.; Yu, H.; Vanysek, P.; Meron, M.; Lin, B.; Benjamin, I.; Schlossman, M. L., Tuning Ion Correlations at an Electrified Soft Interface. *Proc. Nat. Acad. Sci. (USA)* **2012,** *109*, 20326-20331.

(17) Luo, G. M., S.; Yoon, J.; Schultz, D. G.; Lin, B.; Meron, M.; Benjamin, I.; Vanysek, P.; Schlossman, M. L., Ion Distributions near a Liquid-Liquid Interface. *Science* **2006,** *311*, 216-218.

(18) Luo, G. M., S.; Yoon, J.; Schultz, D. G.; Lin, B.; Meron, M.; Benjamin, I.; Vanysek, P.; Schlossman, M. L., Ion Distributions at the Nitrobenzene-Water Interface Electrified by a Common Ion. *J. Electroanal. Chem.* **2006,** *593*, 142-158.

(19) Bu, W. Y., H.; Luo, G.; Bera, M. K.; Hou, B.; Schuman, A. W.; Lin, B.; Meron, M.; Kuzmenko, I.; Antonio, M. R.; Soderholm, L.; Schlossman, M. L., Observation of a Rare Earth Ion-Extractant Complex Arrested at the Oil-Water Interface During Solvent Extraction. *J. Phys. Chem. B* **2014,** *118*, 10662-10674.

(20) Bu, W. M., M.; Amoanu, D.; Lin, B.; Meron, M.; Kuzmenko, I.; Soderholm, L.; Schlossman, M. L., X-Ray Studies of Interfacial Strontium-Extractant Complexes in a Model Solvent Extraction System. J. Phys. Chem. B 2014, 118, 12486-12500. *J. Phys. Chem. B* **2014,** *118*, 12486-1250.