

ELECTROCHEMICALLY DEPOSITED SILVER NANOSTRUCTURES ON REDUCED GRAPHENE OXIDE HYDROGELS AS SENSITIVE SERS SUBSTRATES

MARYAM AGHILI

Surface-enhanced Raman scattering (SERS) is an analytical technique widely used for fast and efficient chemical detection. In this study, we explored the potential of graphene derivatives to serve as support for SERS-active structures. We present a facile method for fabricating 3D SERS substrates by electrodepositing nanostructured silver (Ag) onto a reduced graphene oxide hydrogel (RGOHg) scaffold. The remarkable SERS effect observed is attributed to the large specific surface area of RGOHg, which enables strong molecular adsorption and provides a high density of SERS hot spots. Our findings suggest that graphene oxide hydrogels hold significant promise as 3D SERS substrates for versatile and ultrasensitive chemical detection applications.

AN ELECTRIC FIELD-ASSISTED SERS SANDWICH ASSAY FOR SENSITIVE DETECTION OF BIOMOLECULES

SHAMIM AZIMI

Surface-based biosensors play a key role in portable diagnostic devices. In those sensors, the detection process is typically controlled by the diffusion of analytes from the bulk of the liquid sample to the surface of the sensor. Target analytes, however, are usually present at very low concentrations, making their detection a challenging task. To address this issue, a concentration amplification mechanism for target analytes can be incorporated into the biosensor surface using AC electrokinetic effects, such as alternating current electroosmosis (ACEO), electrothermal fluid flow (ETFF), and dielectrophoresis (DEP). This approach can lead to high sensitivity, low detection limits, and fast turnaround times.

In this study, we developed an effective surface-enhanced Raman scattering (SERS) assay that utilizes electrokinetic forces to deterministically transport and capture analytes from the bulk solution onto the detection surface. By depositing a layer of silver (Ag) nanoparticles on the captured target molecule, a sandwich assay is formed, resulting in a high density of hotspots and enhancing the signal intensity of the analyte by at least one order of magnitude. Our assay provides a promising platform for rapid, reliable, and sensitive in situ monitoring of biomolecules in various bodily fluids, such as blood, urine, and saliva, within a practical range of fluid conductivity.

SELECTIVE GLYCEROL OXIDATION TO FORMATE USING CARBON-BASED ELECTRODE WITH NICKEL AND COPPER CATALYST

MOHAMMADREZA AZARSHAB

The biodiesel production process generates glycerol as a by-product, which typically comprises 10% of the total weight. However, the price of crude glycerol has recently decreased significantly, causing an oversupply in the global market and reducing profitability for the biodiesel industry. To address this issue, glycerol can be converted into high-value products to increase profit margins. One promising product is formate, which can be produced via Glycerol Electro Oxidation Reaction (GOER). However, limitations such as the use of expensive precious metals like platinum and gold for electrode preparation, low electrochemical performance, and poor selectivity have hindered the process. Ni-based catalysts have been used for glycerol oxidation to formic extensively, but often suffer from low selectivity. Here, we found that combining Ni with Cu significantly improved formate production selectivity, reaching a Faradaic efficiency of 97% to gain a current density of 5mA/cm² at a potential of 1.42 V vs. RHE. This research has significant applications in facilitating energy generation in electrochemical processes, such as employing GOER as an anodic reaction for improving H₂ production in water splitting, or enhancing power generation for direct alcohol fuel cells (DAFCs).

DISTRIBUTED EXTREMUM-SEEKING CONTROL WITH NONLINEAR GAIN FOR A CLASS OF OPTIMIZATION PROBLEMS

SONIA BATTISTA

We propose a distributed extremum seeking controller with a nonlinear gain to solve a class of real-time optimization problems. Each dynamic agent in the network has unknown dynamics, and it is assumed that each agent knows only its own local cost measurement. The nonlinear gain term makes the practical implementation of the controller more feasible. It ensures the gain is large enough to achieve convergence to the optimum and eliminates the issue of tuning the controller gain. The proposed method is illustrated using a simulation example.

SCALABLE ROUTES TO BLOCK COPOLYMERS VIA CU-MEDIATED REVERSIBLE DEACTIVATION RADICAL POLYMERIZATION

HAYDEN DEACON

Cu-mediated Reversible Deactivation Radical Polymerization (RDRP) has been investigated as a method to produce (meth)acrylic polymers of high chain-end functionality and well-defined structure, enabling the production of uniform block copolymer materials. The use of relatively inexpensive reagents with common, simple, and scale-appropriate reactor configurations are key features in overcoming the hurdles to commercialization. To that end, a previously-developed two-step process that produced a poly(methyl acrylate) (PMA) macroinitiator species continuously in a copper tubular reactor that was subsequently chain-extended in a semi-batch reactor was investigated. The complexing ligand N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) utilized in the chain-extension step is significantly less costly than other commonly used ligands such as tris[2-(dimethylamino)ethyl]amine (Me₆TREN), while conducting the chain-extension in semi-batch offers an effective means to manage polymerization exotherms at larger scales. Previous studies have demonstrated success in chain-extending with acrylates, however slow polymerization rates and poor initiation efficiency is observed with methacrylates.

Using methyl acrylate (MA) as a model system, reaction conditions and feeding strategies were optimized to accelerate polymerization in the semi-batch system, leading to a 2-fold reduction in reaction time with no loss in control compared to previous studies of this system. It was concurrently demonstrated that pre-polymerization in copper tube reactor could be eliminated while still providing a chain-extendible species, a result that simplifies reactor operation, offers greater flexibility in initiator choice, and improves compositional control of the final product. Learnings from the acrylate system were applied to the polymerization of methyl methacrylate (MMA) and di(ethylene glycol) methyl ether methacrylate (DEGMEMA), with the elimination of the PMA macroinitiator and substitution of the initiator methyl 2-bromopropionate (MBP) with ethyl α -bromoisobutyrate (EBiB) providing significant improvement in the initiation efficiency over those observed in previous studies. The conditions developed for the homopolymerization systems were then applied to produce acrylate-acrylate and acrylate-methacrylate block copolymers, also exploring the influence of block order. Reactions with high inter-block conversion were completed in 4 h or less with no intermediate purification or additional catalyst, thus yielding a scalable method of producing block copolymer materials.

PERFORMANCE PREDICTION OF ANAEROBIC DIGESTION OF PULP AND PAPER SLUDGE COUPLED WITH HYDROTHERMAL PRE-TREATMENT USING MACHINE LEARNING ALGORITHMS

MARYAM GHAZIZADE FARD

Effluents from pulp and paper (P&P) manufacturing mills as well as primary and secondary sludge from wastewater treatment plants contain large amount of organics. The high organic load of these waste streams makes it suitable for anaerobic digestion (AD) treatment. However, the first stage of AD, hydrolysis, takes place slowly as the conversion of macromolecules to soluble monomers is typically the rate limiting step.. Hydrothermal pre-treatment (HTP) is a method to accelerate the hydrolysis and the overall AD rate as it breaks large polymer chains into smaller molecules. This would increasing organic solubilization, which improves AD performance including methane production rate and extent. Finding optimum conditions such as temperature, pressure, and residence time to achieve maximum COD solubilization is critical for the process of HTP.

Reviewing the published literature has revealed that the use of AD technology for the P&P industry is limited to a few studies and, therefore insufficient data is available for digestion of solid residues and sludge generated from these facilities. The closest substrate to P&P sludge is waste-activated sludge, for which the feasibilities of HTP application before the AD process has been demonstrated in literature. This project aims to model the results of previously published works on HTP of both waste activated sludge and P&P sludge to determine the optimum conditions along with produce a predictive model that can forecast the result of various scenarios. Three machine learning algorithms, namely random forest, extreme gradient boosting, and deep learning are evaluated for their feasibility of predicting the performance of HTP on the operating parameters collected in published articles on waste-activated sludge and P&P sludge (total of ~750 data points). The accuracy in predicting model outputs, such as methane production, is evaluated for each method by calculating the root mean squared error (RMSE) and mean absolute percentage error. This study demonstrates the potential of using machine learning algorithms to model AD coupled with HTP.

AUTONOMOUS NAVIGATION AND STATION-KEEPING OF HIGH-ALTITUDE BALLOON PLATFORMS

TELEMA HARRY

Unmanned high-altitude balloon platforms (HABP) are flexible structures designed to carry a large payload to the stratosphere for an extended period. They have many real engineering/ scientific applications such as near-space experiments, military surveillance, meteorological observations, and high-speed broadband internet. One of the major challenges of HABPs operation is the autonomous navigation and station-keeping of the balloon for an extended period, as their dynamics depend on wind speed, solar elevation, sparse wind measurements and forecast error. In this work, we are proposing a data-driven real-time optimization and control methodology for the autonomous control and station-keeping of HABPs. The algorithm uses real-time data to compute the gradient with respect to the position and estimates the altitude with a favourable wind profile. Unlike traditional methods, our algorithm does not require lots of historical data to be functional. Using actual wind data from the National Oceanic and Atmospheric Administration (NOAA), we shall illustrate the effectiveness of our proposed algorithm.

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC NANOPARTICLES FOR IN VIVO DRUG DELIVERY

MANPREET KAUR

Gene therapy has generated considerable interest due to its ability to resolve a problem at its source by delivering nucleic acids to modify a cell to produce/alter a specific protein expression. However, these nucleic acids need to be protected by drug delivery carriers to overcome physiological barriers including biodistribution, stability to biological fluids, cellular uptake, endosomal escape, and cytotoxicity. Among other classes, polymeric nanoparticles have been proven to be highly efficient for gene therapy.

This study focuses on the preparation of polymeric nanoparticles for the safe and efficient administration of genetic therapeutics. The proposed goal is to use poly(β -amino acids) (PBAEs) for the synthesis of polymeric nanoparticles by exploring various surface and structural modifications. PBAEs are a class of polymers synthesized via Michael addition of acrylates and amines in an organic solvent without the production of any by-products. These polymers possess various advantages including biocompatibility, biodegradability, pH responsiveness, and facile tunability of structures. The acrylate backbone of PBAEs is responsible for their biodegradability and tertiary amines make these materials pH responsive. This presentation will provide insights into the basic mechanism behind drug delivery to the cell using polymeric nanoparticles and the synthetic route of PBAEs. Preliminary characterization results provide baseline knowledge for further modifications to enhance *in vivo* properties of these polymeric nanoparticles.

PIECEWISE-LINEAR δ -APPROXIMATORS FOR LOWER-BOUNDING NON-CONVEX GLOBAL OPTIMIZATION PROBLEMS

KODY KAZDA

Global optimization is concerned with finding the best element out of a set of possible elements, according to some criterion. We formulate this problem as a mathematical program as follows:


$$\begin{aligned} \min f(x) & \quad (P) \\ \text{s.t. } y_i &= h_i^{NL}(x), \quad i = 1, \dots, m \\ & (\mathbf{y}, \mathbf{x}) \in \mathcal{S} \end{aligned}$$

where without loss of generality $f(x)$ is an affine function referred to as the objective functions, and \mathcal{S} can be a non-convex or convex set. $X = \{(x, y) \in \mathcal{S}: y_i = h_i^{NL}(x), \forall i = 1, \dots, m\}$ defines the set of possible element, referred to as the feasible set. GO seeks to solve (P) by finding the global minimum $x^* \in X$ such that $f(x) \geq f(x^*) \forall x \in X$. The difficulty of finding the global optimum of (P) is that X often possesses a very large or an infinite number of elements, so enumerating all elements is intractable. We must therefore devise algorithms that can rule out elements of X without directly computing their objective value.

GO algorithms rely on the convexity of X to avoid directly consider all elements in X . If X is known to be convex, then any local minimum of (P) is known to also be a global minimum of (P) . Thus, convexity allows local information to infer global information over the entire set of possible elements.


GO is more challenging in the cases where X is non-convex, as it is in many practical process system applications. In this case, X can be partitioned into X_i where $\bigcup_{i=1}^N X_i = X$. Every X_i can be replaced with a convex relaxation $X_i^c \supset X$ to form (P_i^c) . Then we can infer that a local optimum of (P_i^c) is also a global optimum of (P_i^c) , and following from $X_i^c \supset X$ is also a lower-bound on the global optimum value of (P_i) . Any feasible solution to (P_i^c) provides an upper-bound on the global optimum value of (P_i) . If the upper-bound of any partition X_i is less than the lower-bound for any X_j $j \neq i$, then we can infer that the global optimum cannot exist in all such X_j and it can be ruled out from consideration.

This inference method is used in all state-of-the-art GO algorithms to rule out X_i and finitely converge to an ϵ -optimal solution x^* such that $f(x) + \epsilon \geq f(x^*) \forall x \in X$.



Ruling out partitions X_i from possibly possessing a global optimum is more likely when a stronger convex relaxation is employed, meaning one that possesses fewer elements outside X_i . Thus, developing methods to produce stronger convex relaxations for arbitrary X is of central interest to GO research.

In this presentation we will demonstrate how piecewise-linear approximations with bounded approximation error can be used to readily generate strong convex relaxations. Through a case study we demonstrate how employing these piecewise-linear approximations can help quickly find global lowerbounds on instances of (P) that represent large scale natural gas transmission networks where the fuel cost of compressor stations is sought to be minimized. We find that employing piecewise-linear approximations allows for finding lower-bounds quicker than state-of-the art commercial GO algorithms, thereby providing direction for more efficient GO algorithms.



MULTI-AGENT CONSENSUS BASED DISTRIBUTED OPTIMIZATION OVER UNDIRECTED NETWORKS WITH TIME VARYING COST FUNCTION

ALI KESHANI

The purpose of this study is to solve the distributed optimization problem of sum of local convex time varying cost functions over an undirected network of agents using modified Newton consensus. We have implemented a long-established method called dynamic inversion to estimate the inverse of local Hessian matrices to avoid direct calculation and reduce computational cost. A robust dynamic average consensus algorithm has been used in the next step to force the system toward reaching consensus at the optimum. Functionality of our method has been proved mathematically and its performance has been assessed by numerical analysis and simulation.

A MODEL-FREE REINFORCEMENT LEARNING DESIGN TECHNIQUE VIA LIE-BRACKET AVERAGING FOR A CLASS OF NONLINEAR SYSTEMS

MARYAM MOHAMADI

In this study, we propose an extremum-seeking control via Lie-bracket averaging approach for the approximation of optimal control problems for a class of unknown nonlinear dynamical systems. This model-free approach combines an extremum-seeking control (ESC) via Lie-bracket averaging approximation with a reinforcement learning (RL) strategy. The proposed learning approach tries to estimate the unknown value function and the corresponding optimal control policy, by using the Bellman equation and set-based leastsquares estimation, which avoids the dual parameterization of the actor-critic methodology for RL. The Lie bracket approximations for ESC is used to approximate the optimal state feedback controller, which provides a model-free approach to avoid the overparameterization of the system's dynamics and the 1 related increase in the estimation bias that happens in typical model-free AC methods. The proposed approach is shown to provide reasonable approximations of optimal control problems without the need for a parameterization of the nonlinear system's dynamics.

NON-COVALENT SURFACE MODIFICATION OF CELLULOSE NANOCRYSTALS USING BLOCK COPOLYMERS

OLGA TORRES ROCHA

The outstanding properties of cellulose nanocrystals (CNC) such as reinforcing ability, adhesion, or unique optical properties due to self-assembly have promoted intensive research from different academic and industrial research groups mainly attributed to CNC can improve mechanical properties such as hardness or strength in composite materials, and also exhibits effective gas barrier behaviour, reducing oxygen or water vapour transmission. However, the main obstacle to the research and development of new CNC-based materials is that the highly hydrophilic surface of CNC makes them incompatible with hydrophobic matrices such as most polymers or organic solvents, limiting the number of potential uses and applications. In this study, we present the initial results of a simple and effective method to modify CNC surface properties using block copolymers.¹ These block copolymers contain a cationic block and a stabilizing block (**Fig. 1**) where the cationic block anchors the chains to CNC via complexation to the anionically-charged CNC surface whereas the stabilizing block stabilizes the CNC with the surrounding media, providing dispersibility in or compatibility with various solvents according on the nature of that block.

This approach is considerably simpler and less expensive than modification approaches based on covalent modification approaches.¹ In this study, the anchor block is based on poly(butyl vinyl imidazole bromide) (PBUVIm) and the stabilizing blocks on poly(styrene) (PS), poly(n-butyl acrylate) (PBA), and poly(polyethylene glycol methacrylate) (PPEGMA). The block copolymers were synthesized via nitroxide mediated polymerization (NMP) a polymerization technique that allows tailoring the degree of polymerization of each block. Block copolymers were synthesized via nitroxide-mediated mediated polymerization which enables tailoring the degree of polymerization of each block. The anchor block is based on poly(butyl vinyl imidazole bromide) (PBUVIm) and the stabilizing blocks on poly(styrene) (PS), poly(n-butyl acrylate) (PBA), and poly(polyethylene glycol methacrylate) (PPEGMA). Modification of CNC with different block copolymers was confirmed via infrared spectroscopy and thermogravimetric analysis. The effect of the nature of the stabilizing block and their corresponding degree of polymerization on the dispersion of polymer-modified CNC in organic solvents and water were evaluated via dynamic light scattering.

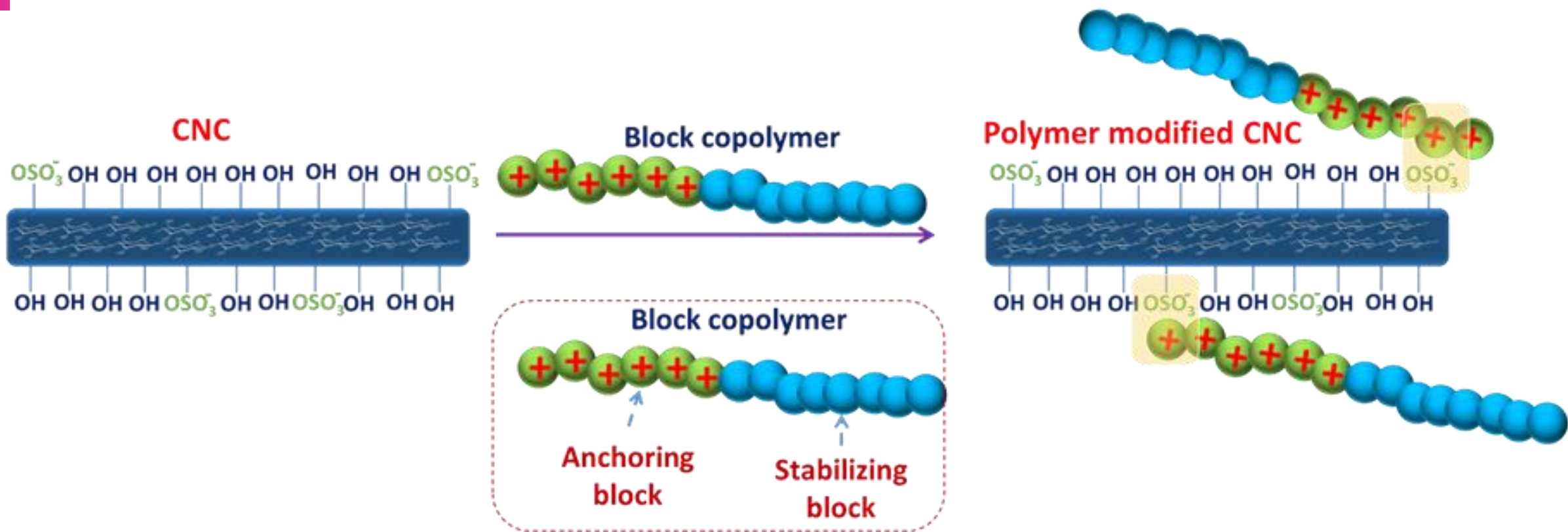




Figure 1. Schematic of the non-covalent functionalization of CNC.

CURIOUS ADVENTURES IN OF BLOCK-RANDOM COPOLYMERS IN AQUEOUS SOLUTION AND THEIR ROLE IN EMULSION POLYMERIZATIONS

CONNOR SANDERS

Amphiphilic *diblock* copolymers of the form *A-block-B* are important materials in the fields of catalysis, drug delivery, colloidal stabilization, sensing, and more. In water, amphiphilic block copolymers are composed of a hydrophobic polymer block (A) and a hydrophilic polymer block (B). The behaviour of block copolymers of this type is analogous to small-molecule surfactants in surface activity, self-assembly into multi-chain structures, and stabilization of colloidal systems. In this work, amphiphilic *block-random* copolymers are composed of hydrophobic polystyrene (PS) and hydrophilic poly(acrylic acid) (PAA) in a slightly different form than a typical diblock copolymer; specifically, *PS-block-(PS-ran-PAA)*. Previous work with block random copolymers has shown they are effective replacements for surfactants in emulsion polymerization (i.e. they provide colloidal stability).



Interestingly, their influence on the mechanisms of emulsion polymerization is unlike any stabilizer applied previously. In this talk, we will explore my work around understanding how the nature of the *PS-block-(PS-*ran*-PAA)* copolymers in aqueous solutions impacts the mechanism of particle formation and growth in emulsion polymerizations. Emphasis will be placed on the self-assembly and interfacial phenomena in aqueous environments. I observe that the pH and ionic strength have strong influence on the size of the self-assembled structures and the adsorption dynamics. This work sets the stage for developing a more thorough picture of the mechanisms operating in emulsion polymerizations stabilized by block-random copolymers.

OPTIMIZATION OF A TERNARY ELECTROLYTE FOR A NON-AQUEOUS VANADIUM HYBRID BATTERY-SUPERCAPACITOR

KATIE SCIBORSKI

Renewable, low-carbon energy sources have attracted considerable interest in recent years. The rise in renewable energy, coupled with its intermittent nature, requires the fabrication of large-scale energy storage systems. Electrochemical energy systems provide an efficient, scalable approach. Generally, electrochemical energy systems are either supercapacitors, utilizing electrical double-layer formation as a mechanism, or batteries/fuel cells, which utilize electrochemical reactions. While batteries have high energy content their power rate is low. Contrastingly, supercapacitors are distinguished by their high-power rates but feature low energy content. We propose a hybrid battery-supercapacitor device consisting of high surface area electrodes paired with a non-aqueous redox electrolyte. The high surface area of the electrodes along with the high voltage operation of the non-aqueous electrolyte allows for supercapacitor operation. The additional redox activity enables the battery features. Thus, the combination of both effects considerably increases the energy density of the hybrid in comparison to a traditional supercapacitor. This seminar is focused on the optimization of the concentrations of supporting electrolyte and active species within the electrolyte mixture.

A CO₂ REGENERABLE WEAKLY BASIC CHEMISORBENT FOR ORGANIC ACID RECOVERY

ALEX TREMBLAY

The development of a P([VC₁₂Im][Cl]_{0.40}[HCO₃]_{0.60}) polyionic liquid functionalized with a weak base for the extraction of organic acids from dilute aqueous solution is analyzed. The reactive bicarbonate functionalized polymer is formed through ion exchange. The equilibrium time for extraction and the total extraction of organic acid at various phase fractions in solution are measured. The initial formation and the one step acidification and regeneration of the reactive polymer using pressurized carbon dioxide is analyzed.