



FILTRATION OF ISOTOPIC WATER MIXTURES WITH GRAPHENE OXIDE (GO) MEMBRANES


ALIREZA BAGHERZADEH HOSSEINABAD

Nuclear plants are a reliable, low-carbon emissions, electric power production source. However, the majority of existing nuclear plants around the world generate radioactive forms of water as by-products, typically HTO or DTO; where “T” is tritium (^3H), and “D” is deuterium (^2H). Tritiated water is radioactive and cannot be released into the environment. This leads to the requirement for the cleanup of thousands of tons of water with moderate activities of tritium. At the present time, the separation of tritiated water from heavy water employs inefficient and energy-intensive methods like water distillation and chemical exchange. The development of an alternative separation method is highly desirable, as it can lead to both environmental and economic benefits. Recently, GO membranes have shown promise in separation of heavy water from light water and have been the subject of several studies.



In the present work, GO membranes are produced through the filtration of water-based GO suspensions using either vacuum-assisted, or pressure-driven filtration. The membranes are subsequently characterized in terms of physical structure and chemical composition with a number of experimental techniques. We use SEM imaging to determine the thickness, structure, and surface features of the GO membranes and XRD to measure the distance between the GO layers. XPS provides us with a distribution of functional groups in GO and the carbon-to-oxygen ratio.

The GO membranes are subsequently tested in terms of their ability to separate isotopic water from light water in a vapour-phase filtration process. Separation efficiencies over 6% in single-pass filtration are obtained from heavy water/light water mixtures. GO membranes produced through pressure-driven filtration show a slightly better separation performance (by almost 1%) but lower permeation flux (by about 20%). The effect of experimental parameters, such as membrane thickness, operating pressure and temperature on separation efficiency is also investigated.



QUANTITATIVE INSIGHTS INTO POLY(ACRYLATE) FORMATION: COMPARING MODEL PREDICTIONS WITH EXPERIMENTAL DATA IN HIGH-TEMPERATURE SEMI-BATCH RADICAL POLYMERIZATION

MAHSA ESMAEILZADEH

Acrylic resins are foundational components for many automotive coatings and adhesives due to their excellent chemical and mechanical properties. Understanding the kinetics of radical polymerization under commercial high temperature semi-batch starved feed conditions operating conditions is a complex task, particularly for acrylate monomers such as butyl acrylate (BA). The influence of secondary reactions on polymer properties and the polymerization rate become crucial. Selection of operating conditions to maximize macromonomer content allows for subsequent chemical modification to produce specialized graft or comb copolymer architectures, thereby increasing the value of acrylate resins. This study aims to refine the kinetic parameters used to model acrylate homopolymerization, with a focus on the reaction network required for prediction of macromonomer content. Using the PREDICI software, a set of kinetic parameters including backbiting, scission, termination, as well as transfer to solvent was estimated.

The refined model improved predictions for not only macromonomer content, but also key variables such as weight-average molar masses (M_w), free monomer concentrations, and molar mass distributions. The modified model was further tested on BA/butyl methacrylate (BMA) and hydroxyethyl acrylate (HEA)/BMA copolymerization systems, demonstrating a good match with experimental data. For further improvement in the model predictions, chain length-dependent termination kinetics was implemented successfully in the acrylate homopolymerization model. The study underscores the utility of parameter estimation to improve representation of this complex system, and opens doors for modeling the polymerization of other acrylates, like isobornyl acrylate (iBoA). The estimated kinetic parameters for iBoA homopolymerization model are lower than those for BA, aligning with our understanding of the two systems.

MODEL-BASED BAYESIAN D-OPTIMAL DESIGN OF EXPERIMENTS IN PHARMACEUTICAL PRODUCTION

LAUREN GIBSON

Mathematical models are important for process design, control, and optimization for different types of chemical systems, but they often contain many unknown parameters that require estimation from experimental data. Model-based design of experiments (MBD_{oE}) can be used to plan experiments that lead to accurate parameter estimates and improved reliability of the model. For nonlinear models with many kinetic parameters, computation of MBD_{oE} objective functions is a challenge due to a singular Fisher information matrix (FIM). Several methods have been developed to overcome the problem of a singular FIM such as parameter-subset selection and Bayesian approaches. In this study, we propose a simplified Bayesian D-optimal approach that makes the FIM invertible by accounting for prior parameter information. A pharmaceutical case study is used to design D-optimal experiments using the proposed Bayesian objective function. We show that the proposed approach leads to improved parameter estimates. Estimates obtained from old data and sequential D-optimal experiments occupy a smaller minimum-volume hyper-ellipsoid than parameter estimates from just old data or from old data and corner-point experiments. The estimates from A-optimal experiments and D-optimal experiments using the simplified Bayesian approach were also compared, confirming that the estimates from D-optimal experiments are better in a D-optimal sense and estimates from A-optimal experiments are better in an A-optimal sense.

MODELING OF A HEAT-INTEGRATED BIOMASS DOWNDRAFT GASIFIER: INFLUENCE OF FEED MOISTURE AND AIRFLOW

HOUDA HAIDAR

A model for a heat-integrated biomass downdraft gasifier is developed and used to study the influence of changes in biomass moisture content and gasifier airflow. This one-dimensional steady-state model accounts for pyrolysis, combustion and gasification reaction kinetics as well as transport phenomena occurring within the gasifier and heat integration system. The gasifier is divided into four zones for solving the ordinary differential equations (ODEs), because each zone has different geometry for the reactor or heating system. The material and energy balance ODEs are solved as a boundary value problem (BVP), ensuring that conditions for the producer gas at the bottom of the reactor match the conditions of the countercurrent annulus gas, which is used for heating. The model also accounts for the preheating of the biomass using exhaust gas from an associated engine used to generate electricity from the producer gas. The model predicts the process gas temperature, flowrate and composition and was validated using two experimental runs with different control inputs. The model predictions show good agreement with the data. Simulations with the highest feed moisture result in lower reactor temperatures and simulations with the highest airflow result in the highest reactor temperatures.

IMPROVED GAIN CONDITIONING FOR LINEAR MODEL PREDICTIVE CONTROL

MOUNA HARB



One challenge when using linear model predictive control (MPC) is that model mismatch and ill-conditioned gain matrices can lead to undesirable aggressive controller behavior. To address this issue, we propose improvements to an existing offline method for gain-matrix conditioning. The proposed algorithm identifies problematic manipulated variables (MVs) with correlated effects on controlled variables (CVs) and solves a constrained linear least-squares optimization problem to adjust the problematic gains. Additionally, the proposed algorithm prevents the optimizer from switching the signs of some gains and allows control practitioners to specify trusted key gains that should be held constant. We also extend the method to condition gain submatrices in scenarios where some of the CVs may temporarily be eliminated from the control problem. To illustrate the effectiveness of the proposed algorithm, we present a case study involving industrial fluidized catalytic cracking.

SUPERCAPACITOR-BATTERY HYBRID BASED ON MULTIVALENT VANADIUM FOR STORAGE OF RENEWABLE ENERGY

EJ JUN LUNG

Batteries have inherent limitations, such as delivering electricity at relatively low current densities and having shorter cyclic durability than supercapacitors. Supercapacitors, known for their high capacity and robust operating limits, excel in handling higher current densities. This motivates the pursuit of a hybrid system that combines the strengths of both batteries and supercapacitors.

This presentation introduces an asymmetric battery-supercapacitor hybrid coin cell device, capitalizing on two distinct charge storage mechanisms: electrical double-layer formation and faradaic reactions. This innovation yields a device with commendable energy capacity at low current densities and exceptional power density at high current densities. Several design aspects will be discussed in this presentation, including details about the electrode material, electrolyte, current collector, the types of membranes, and hydrophilic surface treatment.



Hybrids are thoroughly characterized with a multitude of techniques. We present results from three-electrode cyclic voltammetry, which is used to identify the redox peaks contributing to the faradic reaction. Additionally, Electrochemical Impedance Spectroscopy measurements are discussed, which demonstrate how the resistivity of hybrids is influenced by the material choices. Finally, galvanostatic charge-discharge characterization and the long-term performance data are presented.

PARAMETER ESTIMATION AND ESTIMABILITY ANALYSIS IN PHARMACEUTICAL MODELS WITH UNCERTAIN INPUTS

IMAN MOSHIRITABRIZI

A methodology is proposed to aid parameter estimation in fundamental models of pharmaceutical processes. This methodology addresses situations with insufficient data to reliably estimate all parameters, when the estimation is complicated by uncertain independent variables. The proposed method uses an augmented sensitivity matrix to rank the combined set of parameters and uncertain inputs from most estimable to least estimable. An updated mean-squared-error criterion is then used to determine the appropriate parameters and inputs that should be estimated, based on the ranked list. A model for one step in a batch pharmaceutical production process with an uncertain initial reactant concentration is used to illustrate the method, revealing that the initial reactant concentration in each batch should be estimated along with three out of six model parameters. Non-estimable parameters are fixed at their initial values to prevent overfitting. The method will aid error-in-variables parameter estimation in many situations involving limited data.

EXTENDING FORMATE PRODUCTION OPERATION TIME FROM CO₂ ELECTROREDUCTION ON SN-BASED CATALYST THROUGH IN-SITU REGENERATION

BEHNAM NOURMOHAMMADI KHIARAK

CO₂ emissions have been attributed to global warming and climate changes. To limit the global warming to 1.5°C, there is a need to remove billion tonnes of CO₂ annually. Electrochemical CO₂ reduction is one of the promising technologies that gives pragmatic solutions for CO₂ mitigation. However, stable CO₂ electrochemical reduction at high current densities, which is closest to industrial practice, has remained challenging due to the competitive hydrogen evolution reaction. In this study, we present highly selective Sn-based catalysts for CO₂ electroreduction to formate at high current densities. These catalysts were prepared by depositing a layer of Sn nanoparticles onto a polymer membrane coated with sputtered Ag. The catalysts exhibited exceptional Faradaic efficiency of over 90% towards formate in the current density range of 50-300 mA.cm⁻² and demonstrated stability for more than 20 hours at a current density of 100 mA.cm⁻². Analysis of the catalysts after 20 hours CO₂ reduction reaction revealed significant morphological changes. To address the need for extended operation time, we developed an innovative in-situ catalyst regeneration strategy. This approach involved periodic oxidation of the catalysts during the reduction reaction, resulting in an extended operation time of the Sn-catalysts to over 150 hours, while maintaining a selectivity of over 90% at a current density of 100 mA.cm⁻². The findings of this study highlight the potential of Sn-based catalysts for efficient and stable CO₂ electrochemical reduction, paving the way for the advancement of sustainable CO₂ mitigation strategies.

HIGH-RATE AND SELECTIVE CONVERSION OF CO₂ FROM AQUEOUS SOLUTIONS TO HYDROCARBONS

CORNELIUS OBASANJO

Electrochemical carbon dioxide (CO₂) conversion to hydrocarbon fuels, such as methane (CH₄), offers a promising solution for the long-term and large-scale storage of renewable electricity. To enable this technology, CO₂-to-CH₄ conversion must achieve high selectivity and energy efficiency at high currents. Here, we report an electrochemical conversion system that features proton-bicarbonate-CO₂ mass transport management coupled with an in-situ copper (Cu) activation strategy to achieve high CH₄ selectivity at high currents. We find that open matrix Cu electrodes sustain sufficient local CO₂ concentration by combining both dissolved CO₂ and in-situ generated CO₂ from the bicarbonate. *In situ* Cu activation through alternating current operation renders and maintains the catalyst highly selective towards CH₄. The combination of these strategies leads to CH₄ Faradaic efficiencies of over 70% in a wide current density range (100 – 750 mA cm⁻²) that is stable for at least 12 h at a current density of 500 mA cm⁻². The system also delivers a CH₄ concentration of 23.5% in the gas product stream.