

Enhanced Graphical Representation of Electrochemical Impedance Data

Electrochemical impedance spectroscopy is well-established as a workhorse technique for evaluating interfacial reactions and electrolyte properties in electrochemical and corrosion science research. Typically, graphical representations of the data in Nyquist and Bode formats are used to get an overall perspective on system behavior and to identify specific key parameters such as polarization resistance, solution resistance, number of time constants, etc. Orazam and coworkers have provided an overview of these traditional graphical formats as well as presenting alternative representations that allow additional insight into system behavior. In many systems the solution resistance dominates the high frequency response, obscuring information that is embedded in the data but often overlooked. Correcting the data to remove this effect results in Bode Magnitude and Phase Angle plots that can provide additional quantitative information about the system; e.g., the alpha parameter for a constant phase element can be easily extracted from the corrected Bode Magnitude plot. The caveat is that gaining a sufficiently accurate value for solution resistance may be difficult or impossible for some systems. An alternative format, plotting the imaginary resistance vs. frequency provides another route to quantifying alpha without an estimate for solution resistance. The authors explore the utility of these formats for both simulated data sets and an experimental data set for an Al-Mg alloy in sodium sulfate.

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Effect of Anions and Oxygen on the Kinetics of the Anodic Dissolution of Nickel

Nitrate, sulfate, and chloride all have a significant impact on the dissolution of nickel. Researchers at the University of Valencia in Spain studied the impact of these species in aerated and deaerated conditions through a combination of basic electrochemical experimentation and a simple kinetic model. The model consists of three reactions – the first is the transition of Ni to Ni(I) plus an electron; the second is the transition of Ni(I) to Ni(II) plus an electron; and the third is the transition of Ni(II) to Ni²⁺aq. At the nickel surface, a gel-like phase forms which contains Ni(I) and Ni(II) compounds, as well as the anions from the bulk electrolyte. The third reaction takes place at the gel-layer/solution interface. Once incorporated into this layer, sulfate ions act as a negative fixed charge, causing the surface film on the nickel to behave as a cation pseudoselective membrane. This results in the accumulation of hydroxyl ions at the surface, favoring formation of Ni(OH)₂ and passivation of the metal surface. Adding chloride causes an increase in the kinetics of the Ni(II) to Ni²⁺ reaction,

resulting in active/passive behavior. When nitrate is present, the resulting hydroxo complexes generated by nickel dissolution act as a positive fixed charge, causing the surface film to behave as an anion pseudoselective membrane. This results in the accumulation of hydronium ions at the surface, in turn stimulating the Ni(II) to Ni²⁺ reaction. The addition of chloride further exacerbates this effect.

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Damage to the Cathode Catalyst of a PEM Fuel Cell Caused by Localized Fuel Starvation

In the last decade, there have been intense efforts to commercialize proton exchange membrane (PEM) fuel cells for various applications, including automotive applications. These efforts have resulted in the identification, and mitigation, of various failure modes during operation. Recently, it was shown that introduction of hydrogen into a fuel electrode that is filled with air, a situation that could occur during start-stop operation, leads to corrosion of the carbon support in the cathode, resulting in performance decay. Patterson and Darling from UTC Fuel Cells in Connecticut show that this failure mechanism can also occur during regular operation due to localized fuel starvation, caused by, for example, water droplet accumulation in the anode gas-diffusion layer or flow fields. The authors fabricated a “model” electrode where a portion of the active area of the anode gas-diffusion layer is blocked off by impregnating the layer with Kynar, thereby simulating localized fuel starvation. The modified electrode was tested in a fuel cell configuration and the changes to the electrode visualized using electron probe microanalysis. Results show severe carbon corrosion in the obstructed regions with the effect being less pronounced closer to the edge of the obstruction. The authors suggest that fuel depletion regions larger than 2 mm can lead to carbon corrosion and performance loss when using pure hydrogen.

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Alcohol Fuel Cells Using CsH₂PO₄ Electrolyte

Implementation of alcohol fuels in fuel cells, energy conversion devices that combine the benefits of zero emissions and high efficiency, requires that the fuel cell electrolyte be impermeable to the fuel. In addition, moderate temperature operation is desirable to minimize CO poisoning at the anode and to enhance fuel electro-oxidation kinetics. Haile and coworkers at the California Institute of Technology have met these requirements by using a solid acid proton-conducting electrolyte, CsH₂PO₄. Continuing their previous work that successfully demonstrated hydrogen/oxygen fuel cells

based on this electrolyte, the authors recently reported a high-power-density alcohol fuel cell based on the same electrolyte, and a Cu-ZnO/Al₂O₃ methanol steam-reforming catalyst integrated into the anode chamber. The temperature of operation, ~250°C, is matched both to the optimal value for fuel cell power output and for reforming. Peak power densities using methanol and ethanol were 226 and 100 mW/cm², respectively. The high power output (305 mW/cm²) obtained from reformate fuel containing 1% CO demonstrates the potential of this approach with optimized reforming catalysts and also the tolerance to CO poisoning at these elevated temperatures. The integrated design is preferable over both direct methanol and reformed methanol systems based on polymer electrolyte membrane fuel cells.

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Copper Electrodeposition and Electrodisolution in Presence of Chloride

The electrochemical reaction for copper dissolution and copper ion deposition is technologically important, especially with the introduction of copper in microelectronic interconnects. A team of researchers from France and Spain revealed more of the copper electrochemical mechanism for the two mono-electron transfers in this reaction, which varies with the participating anion. The mass change per unit charge function was derived from the combined quartz crystal microbalance and cyclic voltammetry experiment to provide information on the species adsorbing or desorbing during the process. For each potential region, the $F\Delta m/\Delta Q$ function evaluated from the data was compared to expected values for selected global processes. These researchers drew several conclusions about possible mechanisms from these comparisons. Copper passivation during deposition in non-deaerated acidic sulfate solution is likely due to oxygen reduction which locally increases the solution pH. The experimental results, agreeing with the literature, indicate that the chloride ion stabilizes the Cu(I) species. Chloride ions in solution influence, whereas dissolved oxygen does not control the copper dissolution mechanism for their experimental conditions. Scan rate dependence experiments provided additional information separating chemical from electrochemical processes. The important advance made by this work is elucidation of the location of reaction intermediates with respect to the working electrode. Future work will include ac electrogravimetry.

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