

Advancing Direct Liquid Redox Fuel Cells: Mixed-Reactant and *In Situ* Regeneration Opportunities

A group of researchers from the University of British Columbia and the National Research Council of Canada has been working on a type of fuel cell referred to as a direct liquid redox fuel cell (DLRFC) in which the air cathode of a regular direct liquid fuel cell is replaced with a metal-ion redox couple over a carbon cathode. The new cathode eliminates the use of platinum group metals, avoids cathode flooding issues, and provides high cathode selectivity and design flexibility. In their most recent work, the authors reported two new approaches in advancing this technology. The first one is the use of mixed-reactant operation that involves supplying a mixed methanol $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox electrolyte only to the carbon cathode. Spontaneous methanol crossover supplies the fuel to the anode. This approach has the potential to significantly improve the cost, compactness, and volumetric and gravimetric power densities of the cell. The second approach is the *in situ* regeneration of the redox couple by supplying air to the methanol anode that then becomes an air cathode, which reverses the direction of electron flow and regenerates the redox couple on the other electrode. The unique feature of this approach is that the regeneration is spontaneous and produces power in contrast to conventional regeneration approaches that require power.

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Electrophoretically Fabricated Diamond Nanoparticle-Based Electrodes

The implementation of nanomaterials into real-world device applications, such as the development of environmentally sustainable fuel cells, has progressed with the recent development that high surface area catalytic materials can be fabricated from nanostructured diamond. Of the multitude of available techniques to control the liquid phase distribution of nanomaterials, electrophoretic deposition appears to be well suited to provide a facile, expeditious path toward the fabrication of uniform nanostructured films. In this vein, scientists from the University of Puerto Rico at San Juan have employed both electrophoretic deposition to deposit films comprised of nanoparticulate diamond and electrochemical deposition to form platinum coatings atop said diamond. These films, cast atop silicon substrates, were fashioned as electrodes in fuel cells and exhibited favorable cyclic voltammetric current profiles for the oxidation of methanol. Further, the scientists confirmed that electrophoretic deposition yields chemically stable electrodes for fuel cell device applications. Future studies of boron-doped nanodiamond systems, which would result in p-type electrodes,

may expand the appeal of these materials and this fabrication technique for other energy storage device applications.

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$\text{Fe}_2\text{O}_3/\text{Fe}/\text{Carbon}$ Nanocomposites for Lithium-Ion Batteries

Lithium-ion batteries are widely used because of their high energy density, low weight, stability over time, and ability to handle hundreds of charge-discharge cycles. Among the most common applications are personal electronic devices such as cellular telephones, laptop computers, and MP3 players. Transition-metal oxides (based on Co, Ni, Fe, etc.) have emerged as potential anode materials because they deliver a specific capacity 2-3 times larger than the currently used graphite. Researchers at the Seoul National University and the Korea Polytechnic University recently reported a study of Fe_2O_3 electrodes that had two major objectives: minimizing the massive volume changes (swelling/contraction) of the Fe_2O_3 electrode, and providing a conduction pathway in the electronically loosened electrode caused by the volume change. They studied three different electrodes (one made from commercial nanosized Fe_2O_3 , a second made from carbon-supported nanosized Fe_2O_3 , and a third from carbon-supported nanosized Fe and Fe_2O_3). They measured cycle retention, rate capability, electrode volume change, and internal resistance properties, and determined that the best overall performance was obtained from the third electrode. The authors concluded that the high electrical conductivity of the carbon and metallic Fe minimized the internal resistance and enhanced the rate capability of the electrode even after the conductive network had been loosened by volume changes associated with electrode operation.

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Improving Electrochemical Performance of LiMnPO_4 Lithium Battery Cathodes with Magnesium Doping

Many commercialized lithium ion batteries use high-cost and toxic cathode materials, such as lithium cobalt oxide (LiCoO_2), and there is demand to substitute these cathode materials with environmentally friendly, low-cost alternatives. Potential alternatives include the olivine-structured phosphates, LiMPO_4 ($M = \text{Fe, Mn, Ni}$), because they exhibit a combination of low cost, nontoxicity, high theoretical capacity, and high electrical and thermal stability. However, cathodes constructed from these olivine-structured phosphates typically demonstrate low electrical and ionic conductivity. The literature reports an improvement in the conductivity of lithium iron phosphate, LiFePO_4 , by selectively doping the material with cations supervalent to lithium. Researchers in Japan applied this cation

doping approach to lithium manganese phosphate, LiMnPO_4 , which has a higher theoretical energy density than LiFePO_4 . The researchers employed a combination of spray pyrolysis and wet ballmilling with heat treatment to prepare various magnesium-doped LiMnPO_4 formulations, $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0, 0.02, 0.04, 0.12$). Comparing the electrochemical impedance spectra of magnesium-doped and non-doped LiMnPO_4 electrodes revealed that magnesium doping improves the lithium ion diffusion and interfacial conductivity. A doping level of $x = 0.04$ demonstrated the highest 0.05C discharge capacity and was a compromise between improved electrode conductivity and a reduction in the number of active manganese ions.

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The Role of Nanostructure in the Electrochemical Oxidation of Model-Carbon Materials in Acidic Environments

Carbon is utilized within numerous electrochemical energy production and storage devices, such as batteries and fuel cells. Under conditions of large applied potentials, high temperatures, and cyclic use, the chemical stability of that carbon can be lost. Degradation of the carbon due to electrochemical oxidation can have a negative impact on the performance of such devices. Currently, there is little understanding of the actual processes involved and how such processes are impacted by the physical structure of the carbon. In this work, a series of model-carbon materials were evaluated to develop an understanding of the impact of presumed oxidation controlling factors, such as the carbon nanostructure, surface chemistry, and impurity content, on the kinetics of the oxidation process. Two distinct oxidation behaviors were identified. First, while the results of this study are too limited to be considered completely definitive, they support the conclusion that the oxidation behavior is a strong function of the magnitude of the inter-graphene layer interactions, with increased bond strength, achieved via thermal processing, as an example, resulting in increased resistance to electrochemical oxidation. Second, the oxidation kinetics were found to be largely independent of common impurities such as iron and sulfur, both of which have previously been suggested as playing a role in the oxidation process.

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