MIXED-CONDUCTING OXIDES IN ELECTROCHEMICAL POWER SOURCES

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Fuel cells, batteries, and pseudocapacitors have been the subject of intense research for decades. The investment in electrochemical power sources continues to grow with the recognition that these electrical conversion and storage devices are clean, efficient sources of power. Professor Worrell deserves high praise for his contributions to the advancement of electrochemical power sources, particularly the discovery and development of new materials with engineered electrical properties.

My graduate research with Professor Worrell focused on the development of a mixed-conducting oxide, yttria-stabilized zirconia with titania (YZTi), for use as an anode in solid oxide fuel cells (SOFCs). Professor Worrell emphasized the importance of transport properties in the efficacy of solid-state ionic materials and has been the inspiration for several subsequent research projects on pseudocapacitors, direct methanol fuel cells (DMFCs) and polymer exchange membrane fuel cells (PEMFCs).

Professor Worrell targeted YZTi as a SOFC anode material with the knowledge that the hydrogen oxidation reaction could be improved if the oxygen-conducting yttria-stabilized zirconia (YSZ) phase were modified to include electronic transport. If this mixed-conducting YSZ were also to have additional catalytic activity, the fuel oxidation reaction would occur over the entire solid-gas interface and not be limited to three-phase reaction zones.

We resolved the electronic-conduction mechanism in $ZrO_2 \cdot 8$ mol% Y_2O_3 having 5 to 10 mol % TiO_2 by correlating its Ti^{3+} concentration to the electrical properties (1). The Ti^{3+} concentration, as studied by electron spin resonance, increased with the amount of TiO_2 in the YSZ, with increasing temperature and with decreasing oxygen partial pressure. These trends are consistent with an n-type conduction mechanism in the YZTi. A percolation model verified the occurrence of electron (small polaron) hopping in the fluorite lattice of YSZ when as little as 3 mol % TiO_2 is present.

In subsequent research at the Naval Research Laboratory (NRL), I continued to study proton-based mixed conductors such as hydrous ruthenium dioxide ($RuO_2 \cdot xH_2O$ or RuO_xH_y). $RuO_2 \cdot xH_2O$ is an effective electrocatalyst for water reduction and chlorine oxidation, and it exhibits pseudocapacitive charge-storage behavior, with a maximum of 700 to 800 F/g at the composition $RuO_2 \cdot 0.5$ mol % H_2O (2). Charge storage in $RuO_2 \cdot xH_2O$ is attributed a double-insertion mechanism of protons and electrons into its structure.

The electrical behavior of bulk $RuO_2 \cdot xH_2O$ indicates that it is a metallic conductor. However, studies of RuO_2-TiO_2 aerogels confirmed that $RuO_2 \cdot xH_2O$ is actually a mixed protonic and metallic conductor (3). Impedance measurements of these microporous, high surface area structures showed primarily protonic conduction.

In continuing research on $RuO_2 \cdot xH_2O$ at NRL, EXAFS was used to show how the RuO_2 structure and its structural water content affect its mixed conductivity (4). Also studied was the high protonic conductivity of $RuO_2 \cdot xH_2O$ and how it contributes to the methanol activity of the Pt-Ru catalysts used in DMFCs (5,6). The mixed-conductivity properties of $RuO_2 \cdot xH_2O$ thin films are being exploited as layers to block methanol from diffusing through the polymer electrolyte in DMFCs (7).

NRL is also pursuing the use of hydrous transition-metal oxides to enhance the catalytic activity of the Pt catalysts used in PEMFC cathodes. By preparing nanoscale mixtures of the hydrous metal oxides and Pt, the Pt activity for oxygen reduction is significantly enhanced. This research suggests that the catalytic activity of the Pt is not the limiting step in the oxygen-reduction reaction, but rather the transport of reactants and products to and from the catalyst lowers its activity.

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