
V.P.28 The Development of Nano-Composite Electrodes for Solid Oxide Electrolyzers

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shown that both a microstructure with porous features and the presence of a catalyst are crucial for good performance. For the air electrode, surface area seems to be the primary factor in determining performance, since cathodes formed from different perovskites, all based on the LaFeO_3 but having widely different ionic conductivities, exhibited similar performance. Finally, model studies of perovskite-YSZ interfaces, involving nanoparticles deposited onto a YSZ(100) crystal, show that interactions between the perovskite and the YSZ surface can cause the perovskite to spread over the YSZ surface following high-temperature calcinations.

Progress Report

Work on SOFC and SOE is being carried out in three general areas: 1) Infiltrated SOFC anodes (the cathode for an SOE); 2) infiltrated SOFC cathodes (SOE anodes); and 3) studies of model systems for understanding perovskite-YSZ interfaces.

Objectives

Electrodes in solid-oxide fuel cells (SOFC) and electrolyzers (SOE) are typically composites of an electronic conductor and the electrolyte material. The objective of this work is to develop a fundamental understanding of how interactions between the various components of the composite affect catalytic and electrochemical performance. Another objective is to use these insights to design nanocomposites that provide stable, high performance for these applications.

Technical Barriers

A major barrier in the development of SOFC and SOE electrodes is the difficulty in preparing composites that are stable to the conditions under which they will be exposed. Under working conditions, the electrode composites are exposed to high temperatures, low $P(\text{O}_2)$, and potentially high electric fields at three-phase boundary sites. At the fuel-side electrode, they can be poisoned by sulfur or carbon formation and damaged by redox cycling. Sintering and solid-state reactions between the components are major problems.

Abstract

Oxide-oxide interfaces for fuel and air electrodes in solid-oxide fuel cells and electrolyzers have been studied using cells in which the ceramic-based electrodes were formed by infiltration of porous YSZ with conductive and catalytic components. For the fuel electrodes, it is

SOFC Anodes/SOE Cathodes

Most of our recent work in this area has focused on developing ceramic-based anodes because of their stability towards sintering and their tolerance towards carbon and sulfur, relative to the Cu-based anodes that we started with.

A particularly interesting material, developed by a collaborator, Prof John Irvine (St. Andrews University), is $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_5$ (LSCM), a perovskite that is stable and conductive under reducing conditions. Ceramic anodes were prepared by infiltration with the nitrate salts to produce composites with 45-wt% LSCM in a 65% porous yttria-stabilized zirconia (YSZ) scaffold. SEM micrographs indicate that the LSCM coats the YSZ pores following calcination at 1473 K. Composites produced in this manner exhibited conductivities at 1073 K of approximately 1 S/cm in air and 0.1 S/cm in humidified H_2 . Although SOFC with LSCM-YSZ anodes exhibited very poor performance at all temperatures, the addition of 0.5-wt% Pd and 5-wt% ceria exhibited maximum power densities at 1073 K of 1.1 W/cm² and 0.71 W/cm² in humidified (3 % H_2O) H_2 and methane, respectively.

To better understand the catalytic requirements of LSCM-YSZ electrodes, fuel-cell performance was measured after the addition of various catalysts to the LSCM-YSZ composite electrodes. The addition of 0.5 to 1-wt% Pd, Rh, or Ni was sufficient to increase the maximum power density of SOFC in humidified H_2 at 973 K from less than 100 mW/cm² in the absence of a

catalyst to above 500 mW/cm². The addition of either 1-wt% Fe or 5-wt% ceria also improved power densities but to a lesser extent. Finally, the use of Pt paste as the current collector increased performance to a similar extent as intentionally adding a catalyst, showing the importance of using inert materials in electrode testing.

Because LSCM has a low ionic conductivity and appears to form a coating over the YSZ, the high electrode performance that we achieved was very surprising; therefore, we made various measurements to understand why this was the case. Scanning electron microscopy (SEM) showed that the LSCM underwent microstructural evolution upon heating and redox cycling. Although the LSCM formed a film on the YSZ scaffold after heating to 1473 K, treating this microstructure at 1073 K in H₂ caused the formation of an interconnected array of ~10nm scale particles, offering an attractive structure with extensive triple phase boundary regions where electrochemical reactions can occur. Thermodynamic measurements (coulometric titration) demonstrated that the reduction of LSCM and La_{0.8}Sr_{0.2}MnO₃ (LSM) occur over a similar range of P(O₂) and that reduction is the likely cause for formation of the microscale array.

SOFC Cathodes/SOE Anodes

Based on the hypothesis that the ionic conductivity of the perovskite is critical in determining the performance of perovskite-YSZ composites when used as the air electrode, we measured the ionic conductivity of LaNi_{0.6}Fe_{0.4}O₃ (LNF) and La_{0.91}Sr_{0.09}Ni_{0.6}Fe_{0.4}O₃ (LSNF), as well as LaFeO₃ with Ba, Sr, and Ca dopants. All of these materials are good electronic conductors and but their ionic conductivity differed by more than 10³. We then tested fuel cells with cathodes made by infiltration of each of these perovskites, followed by calcinations to either 1123 K (at which temperature each of the perovskites formed small particles on the YSZ scaffold) or 1373 K (at which temperature each formed a film). None of the perovskites underwent solid-state reactions with the YSZ at 1373 K. The performance of the fuel-cell electrodes was found to be indistinguishable for each of the perovskites, raising the question concerning whether ionic conductivity really is a limiting factor in cathode performance.

To determine whether the addition of infiltrated catalysts could influence the performance of cathodes, we examined the effect of adding various dopants to composite cathodes prepared by infiltration of either LSF or La_{0.8}Sr_{0.2}MnO₃ (LSM) and calcined to either 1123 or 1373 K. The addition of dopants had little influence on the 1123-K composite electrodes but all dopants tested improved the performance of the 1373-K composites. With 1373-K, LSF-YSZ electrodes, the open-circuit impedances decreased dramatically following the addition of 10-wt% YSZ, 0.5-wt% Pd,

10-wt% Ce_{0.8}Sm_{0.2}O_{1.9} (SDC), 10-wt% CaO, and 10-wt% K₂O. Similarly, the 1373-K, LSM-YSZ electrodes were enhanced by the addition of 10-wt% CeO₂, 1-wt% Pd, and 10-wt% YSZ. Since the improved performance was close to that of the corresponding LSF-YSZ and LSM-YSZ electrodes that had been calcined to only 1123 K, we concluded that the improvement was related to structural changes in the electrode, rather than to improved catalytic properties or ionic conductivity.

Model Perovskite-YSZ Interfaces

The interaction between LSM nanoparticles and a YSZ(100) crystal was investigated in order to understand the structural changes that occur with increasing annealing temperature. Measurements were performed using AFM, XPS, and SEM/EDX. After depositing nanoparticles of LSM directly onto YSZ(100), samples were annealed from 1123 to 1523 K. The particles gradually decreased in height and eventually disappeared completely. Subsequent reduction in H₂/H₂O at 973 K resulted in the reappearance of nanoparticles. Studies were carried out on identical regions of the sample allowing the same nanoparticles to be characterized at different temperatures. Morphological changes indicate the formation of a thin layer of LSM, and XPS results support that observation by indicating an increase in signal from the La and Sr and a decrease in signal from the Y and Zr with increasing temperature. SEM/EDX was used to verify that the nanoparticles in the reduced sample contained La. The changes in the LSM/YSZ morphology may be important in explaining the non-stationary behavior observed in operating fuel cells.

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