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The stability of lanthanum strontium vanadate for solid oxide fuel cells

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HIGHLIGHTS

- ► Poor redox stability of the anode based on $La_{0.7}Sr_{0.3}VO_3$ (LSV) with a Pd catalyst.
- ► Deactivation of a Pd-catalyst due to the molten phase from LSV in oxidized condition.
- ► Improvement of the redox stability using the V-deficient LSV.

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ABSTRACT

The deactivation upon oxidative treatments of solid oxide fuel cell (SOFC) anodes based on $La_{0.7}Sr_{0.3}VO_{3.85}$ with a Pd/ceria catalyst is examined using electrodes formed by infiltration of $La_{0.7}Sr_{0.3}VO_{3.85}$, Pd, and ceria into porous yttria-stabilized zirconia (YSZ). Based on XRD results, performance measurements of cells made with varying La:Sr:V ratios, and Pd dispersion measurements using CO adsorption, we conclude that $La_{0.7}Sr_{0.3}VO_{3.85}$ is kinetically unstable upon reduction-oxidation treatments at 973 K, forming molten, strontium–vanadate phases that partially cover the catalytic component. Deactivation can be minimized using V-deficient compositions.

1. Introduction

Although state-of-the-art, solid oxide fuel cells (SOFC) are usually based on a composite of Ni and the electrolyte material, typically yttria-stabilized zirconia (YSZ) [1,2], there would be significant advantages in replacing the Ni with a ceramic conductor if comparable electrochemical performance could be achieved. Ceramic conductors would likely exhibit improved redox stability, better tolerance to sulfur poisoning, and better resistance toward coking in the presence of hydrocarbons [3,4]. Finding ceramic replacements for Ni, however, is challenging since the ceramic must remain stable and exhibit high electronic conductivity over the wide $P(O_2)$ range that can exist in the anode compartment. The ceramic anode must also resist reaction with the electrolyte at temperatures required for cell fabrication and exhibit catalytic activity for oxidation of the fuel. Finally, electrode fracture can be a problem if the electrode expands or contracts relative to the electrolyte due to differences in the Coefficient of Thermal Expansion (CTE) or due to changes in volume due to reduction.

The problems of solid-state reaction and differences in the relative expansion with respect to the electrolyte can be addressed by using infiltration methods to prepare the cell electrodes [5,6]. This synthesis procedure involves making a porous scaffold of the electrolyte material together with the dense electrolyte, then infiltrating the electronic conductor and a catalyst into the pores of the scaffold [7]. Contact between the electrolyte and electrode materials need not occur until after all high-temperature processes have been completed. The mechanical properties of composites formed by infiltration, such as CTE, are largely determined by the scaffold material, which is the same as that used for the electrolyte [5]. A number of different ceramic anodes have been prepared in this way, including ones based on $La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) [7,8], $La_{0.3}Sr_{0.7}TiO_3$ (LST) [9–11], $SrMoO_3$ [12], $NaWO_3$ [13], $La_{0.7}Sr_{0.3}VO_{3.85}$ [14,15], and $Ce_{0.7}Sr_{0.3}VO_{3.85}$ [13,16]. Because none of these oxides has catalytic activity approaching that of Ni for oxidation reactions, it is necessary to also add a catalytic metal, in dopant quantities, in order to reduce polarization losses [14,17].

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Among the oxides tested in our laboratory, the vanadates exhibit some of the best overall properties. Unlike $SrMoO_3$ [18], vanadates undergo reduction to their conductive phases at relatively high $P(O_2)$, similar to that required for reduction of NiO [19]; and they cannot be over reduced at lower $P(O_2)$, as in the case of $NaWO_3$. They have electronic conductivities that are at least an order of magnitude higher than that of LSCM or LST under practical SOFC anode conditions, with bulk conductivities reported to be well over 100 S cm^{-1} [20]. In an earlier study, we showed that the conductivity of an $La_{0.7}Sr_{0.3}VO_{3.85}$-YSZ composite with only 10-vol.% $La_{0.7}Sr_{0.3}VO_{3.85}$ is 1 S cm^{-1} at 973 K, sufficiently high to make ohmic losses in the anode composite negligible [14]. As with other ceramic conductors, low anode polarization losses are only observed after the addition of transition-metal dopants [7,14], demonstrating that $La_{0.7}Sr_{0.3}VO_{3.85}$ is not a good electrocatalyst.

Unfortunately, fuel cells made from $La_{0.7}Sr_{0.3}VO_{3.85}$-YSZ, with 0.5-vol.% Pd and 2.3-vol.% ceria as the catalyst, exhibited large increases in their polarization losses after a single oxidation–reduction cycle [14]. Since this treatment did not change the ohmic losses significantly, it would appear that the catalytic component of the electrode was lost. Although catalyst sintering can be a problem with low metal loadings after high-temperature treatments, no comparable losses were observed following similar treatments with anodes based on LSCM [7] or LST [11] and oxidation cycles should actually improve the dispersion of the Pd catalyst [21]. Interestingly, the use of a V-deficient vanadate, $La_{0.7}Sr_{0.3}V_{0.9}O_{3.85-\delta}$, minimized the loss in performance following this redox treatment [14,22]. Because the ability to periodically oxidize the anode is a primary advantage for using ceramics, it is important to understand the reasons behind the deactivation of LSV-based electrodes and to determine what can be done to prevent deactivation from occurring.

In the present study, we investigated the deactivation of the vanadate-based anodes in more detail. We discovered that deactivation upon redox cycling of $La_{0.7}Sr_{0.3}VO_{3.85-\delta}$-YSZ electrodes is due to the instability of the vanadate, which results in the formation of small amounts of a molten phase, $Sr_2V_{2+\chi}O_{7+\delta}$ $(0 < \chi < 1.02)$ that covers the Pd catalyst. The use of V-deficient LSV minimizes the formation of the molten phase, so that the electrode performance is maintained.

2. Experimental procedure

The SOFC button cells in this study were prepared using the same methods described in previous work [14]. Briefly, the first step involved preparation of YSZ wafers, each having a dense layer, 70–80-μm in thickness, with 40-μm porous layers on both sides. These were fabricated by tape casting and lamination, using graphite pore formers for the porous layers. The wafers were calcined to 1773 K before the electrode components were added to the porous layers by infiltration. The outside layers had a porosity of approximately 65 vol.%, with a sponge-like structure and typical pore dimensions between 1 and 3-μm. The diameter of the dense layer was 1 cm but the diameter of the porous regions used for both electrodes was only 0.67 cm. The $La_{0.8}Sr_{0.2}FeO_3$ (LSF)-YSZ cathodes were prepared by infiltration into one of the porous layers using the nitrate salts and procedures described in other papers [23]. The final loading of LSF was 20 vol.% and the final calcination step was 1123 K.

The anodes were prepared by infiltration of the $La_xSr_yV_zO_\delta$ ($L_xS_yV_z$) phase into the porous layer opposite the cathode. The precursor solutions for synthesizing $L_xS_yV_z$ used $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa Aesar), $Sr(NO_3)_2$ (99.9%, Alfa Aesar), and NH_4VO_3 (99%, Alfa Aesar) in distilled water, with the addition of citric acid (100.7%, Fisher Scientific) in the amount of 1 mol per mole of metal cations. After infiltration of the salt solutions, the $L_xS_yV_z$ phase was formed by calcination at 973 K in air. The loading of the $L_xS_yV_z$ phase was 10-vol.% in all cases except the $L_1S_0V_z$; we used 20-vol.% of $L_1S_0V_z$ due to the lower conductivity of the undoped material [20]. Next, CeO_2 (1 M $Ce(NO_3)_3$, Alfa Aesar, 99.5%) and Pd (0.45 M Tetraammine palladium(II) nitrate solution, Alfa Aesar, 99.9%) were infiltrated into the $L_xS_yV_z$-YSZ, followed by heating in air to 723 K, to achieve a loading of a 2.8 vol.% CeO_2 and 0.5 vol.% Pd. In one case, Pt (0.24 M Tetraammine platinum (II) nitrate solution, Alfa Aesar, 99.9%) was used in place of Pd.

To measure performance, the cells were mounted onto an alumina tube using a ceramic adhesive (Ceramabond 552-VFG, Aremco); Ag wire and Ag paste (#05063-AB, SPI supplies) were used for current collection on both sides. While the cathode was simply exposed to the atmosphere, humidified (3% H_2O) H_2 was passed over the anode at a flow rate of approximately 1 mLs^{-1}. The *V–i* polarization curves and impedance spectra were measured using a Gamry Instruments potentiostat. Impedance spectra were measured with a −0.1-V bias from the open circuit voltage (OCV), in the frequency range from 100 kHz to 0.01 Hz, with a 20-mV AC perturbation.

Prior to the initial electrochemical measurements, care was taken to avoid heating the combined catalyst and $L_xS_yV_z$ phase above 723 K in air. For the electrochemical tests, the anodes were heated from room temperature to their operating temperature in humidified H_2. In order to see the impact of oxidizing these two components together, the following experiment was performed. After testing the electrodes at 973 K in humidified H_2, the anode compartment was first flushed with He, then exposed to flowing air for 1 h at 973 K, and again flushed with He before testing in humidified H_2.

Physical characterization of the anode composites was carried out by scanning electron microscopy (SEM) (FEI Quanta 600 ESEM) and X-ray diffraction (XRD) using Cu K_α radiation. To determine the Pd surface areas (Pd dispersion), CO adsorption was performed on composite slabs (4 mm × 4 mm × 15 mm) prepared using identical procedures to that used in preparing electrodes, except that no ceria was added. For measurements on samples referred to as "oxidized", the Pd was reduced at only 723 K. CO adsorption uptakes were measured volumetrically at room temperature and dispersion was calculated by assuming a stoichiometry of one CO molecule per surface Pd. Pure $L_xS_yV_z$ powders were prepared for some of the XRD studies.

3. Results and discussion

The electrochemical performance of cells with $L_{0.7}S_{0.3}V_1$-YSZ composite anodes exposed to humidified H_2, with identical cathodes and electrolytes, has been discussed in detail elsewhere [14]. At 973 K, there was sufficient conductivity with 10-vol.% $L_{0.7}S_{0.3}V_1$ to ensure that ohmic losses in the cell were equal to that expected from the 80-μm YSZ electrolyte, 0.4 Ω cm^2. However, the non-ohmic losses were strongly affected by the addition of the CeO_2 and Pd catalysts. In the absence of an added catalyst, the cells exhibited large non-ohmic losses, ∼2.5 Ω cm^2, and a maximum power density of only 90 mW cm^{-2}. Addition of a Pd/ceria catalyst decreased the non-ohmic losses to ∼0.2 Ω cm^2 and increased the maximum power density to 470 mW cm^{-2}. Although Pd was sufficient for decreasing the non-ohmic losses in the cell without ceria, the addition of both ceria and Pd led to better performance at high current densities [24]. The open-circuit voltage (OCV) was unaffected by the addition of the Pd/ceria catalyst.

Fig. 1 shows *V–i* curves and impedance spectra for a similar cell used in the present study, before and after treatment in air. The anode in this cell again consisted of 10-vol.% $L_{0.7}S_{0.3}V_1$, 2.8-vol.%