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Physical and electrochemical properties of alkaline earth doped, rare earth vanadates

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The effect of partial substitution of alkaline earth (AE) ions, Sr^{2+} and Ca^{2+}, for the rare earth (RE) ions, La^{3+}, Ce^{3+}, Pr^{3+}, and Sm^{3+}, on the physical properties of $REVO_4$ compounds were investigated. The use of the Pechini method to synthesize the vanadates allowed for high levels of AE substitution to be obtained. Coulometric titration was used to measure redox isotherms for these materials and showed that the addition of the AE ions increased both reducibility and electronic conductivity under typical solid oxide fuel cell (SOFC) anode conditions, through the formation of compounds with mixed vanadium valence. In spite of their high electronic conductivity, $REVO_4$-yttira stabilized zirconia (YSZ) composite anodes exhibited only modest performance when used in SOFCs operating with H_2 fuel at 973 K due to their low catalytic activity. High performance was obtained, however, after the addition of a small amount of catalytically active Pd to the anode.

1. Introduction

Solid oxide fuel cells (SOFC) are of interest due to their ability to achieve both high energy conversion efficiencies and power densities. Much of the current research on SOFCs is focused on improving electrode performance to allow either operation at lower temperatures or to increase fuel flexibility. The standard anode in a SOFC is composed of a composite of Ni and the O^{2-} anion conducting yttria-stabilized zirconia (YSZ) electrolyte. These Ni/YSZ cermet electrodes can be very efficient, but have low fuel flexibility and are restricted to use with H_2 or syn gas fuels. The desire for anodes with increased fuel flexibility that will not deactivate via coke formation when exposed to hydrocarbons has motivated research into using conductive ceramics to replace the Ni components in SOFC anodes [1–7]. While some progress has been made in achieving this goal using mixed oxides based on titanates [8–11], manganates [12–15], and chromates [16] (e.g., $(LaSr)TiO_3$ and $(La,Sr)_x(Cr,Mn)_yO_{3-\delta}$) with the perovskite structure, these materials have only modest bulk electronic conductivities (<5 S cm^{-1}) under typical SOFC anode operating conditions. When used in a porous perovskite–YSZ composite anode, the overall conductivity is 1–2 orders of magnitude lower. Thus, for these materials to be used in SOFC anodes, the electrode must be very thin (<50 μm) in order to limit ohmic losses or the perovskite must be restricted to a thin functional layer near the electrolyte. For example, a 45 wt% infiltrated, porous $La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_3$–YSZ composite has a electrical conductivity of only 0.1 S cm^{-1} in humidified H_2 at 973 K [12]. Recently, more highly conductive oxides such as $SrMoO_3$ [17] and $Na_xWO_{3-\delta}$ [18] bronzes, which have bulk conductivities approaching 1000 S/cm, have also been suggested for use in SOFC anodes; however, they appear to be chemically unstable under typical SOFC anode operating conditions.

Rare earth (RE) vanadates (REV_4), such as $CeVO_4$, are another class of oxides that can have high electronic conductivities under some conditions and are chemically stable in a variety of fuels including H_2, H_2S, and CH_4 [19–21], and, therefore, show some promise for use in SOFC anodes. Cerium (III) orthovanadate, $CeVO_4$ has a zircon-type structure which consists of VO_4 tetrahedra sharing corners and edges with CeO_8 dodecahedra [22]. The tetragonal zircon structure stabilizes the Ce^{3+} ion under oxidizing conditions [23]. Upon exposure to reducing environment, a zircon to perovskite phase transition occurs, forming $CeVO_3$ [19, 24]. Recently, Petit et al. studied the redox and electrical properties of $CeVO_4$ under reducing conditions [20, 21, 25, 26] and found that the substitution of a portion of the trivalent Ce ions with divalent alkaline earth (AE) ions significantly enhanced electronic conductivity with a bulk conductivity as high as 12 S cm^{-1} at 973 K being reported for $Ce_{0.6}Ca_{0.4}VO_3$ [20,21]. The conductivity of the $RE_xAE_{1-x}VO_3$ ($REAEV_3$) compounds increases with increasing AE substitution up to the solubility limit. Petit et al. and Watanabe et al. reported the solubility limit of Ca and Sr in the parent $CeVO_4$ corresponds to x values of 0.41 and 0.21, respectively, for materials synthesized by

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sintering the constituent binary oxides at 1273 K [23, 25, 26]. Secondary $Sr_2V_2O_7$ and $Ca_2V_2O_7$ phases are observed at higher AE concentrations [25, 26].

In the present study, we have investigated the physical and electrochemical properties of a range of $RE_xAE_{1-x}VO_{4-0.5x}$ ($REAEV_4$) where RE=La, Ce, Pr, and Sm, that have potential for use in SOFC anodes. In contrast to previous studies, a solution based Pechini method was used to synthesize the vanadates thereby allowing them to be produced at lower temperatures and with higher concentrations of AE (Ca, Sr) ions. The conductivity and the electrochemical performance of $REAEV_3$–YSZ composites that were produced using wet infiltration of the vanadates into a pre-sintered porous YSZ electrode scaffold are also reported.

2. Experimental

The REV_4 materials were prepared using an aqueous precursor solution containing the appropriate amounts of NH_4VO_3 (Aldrich, 99+%) with either $La(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%), $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.5%), $Pr(NO_3) \cdot xH_2O$ (Alfa Aesar, 99.9%), or $Sm(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%). Citric acid (Fisher Scientific) was also added as a complexing agent to aid in the formation of a single phase at a lower temperature. The precursor solution was then dried and the resulting powder was calcined at 973 K in air to form the REV_4. Perovskite $REVO_3$ (REV_3) materials were produced by reducing the REV_4 in humidified H_2 (3% H_2O) at 973 K. $REAEV_4$ oxides were synthesized in the same way as the REV_4, with addition of $Sr(NO_3)_2$ (Alfa Aesar, 99%), or $Ca(NO_3)_2 \cdot 4H_2O$ (Alfa Aesar, 99%) to the precursor solution.

Porous YSZ slabs into which 30 wt% of the REV_4 had been infiltrated were used for conductivity measurements. The porous, 4 mm × 4 mm × 15 mm YSZ slabs were prepared using methods that have been described in detail previously [27, 28]. The REV_4 was added to the porous YSZ slabs by infiltrating the aqueous precursor solution followed by drying and annealing in air at 973 K. Multiple infiltration/annealing cycles were used to obtain the desired 30 wt% loading. For conductivity measurements, the REV_4/YSZ composites were first pre-reduced at 973 K in humidified H_2 (3% H_2O) for 2 h. The conductivity was measured using the 4-probe, DC method with the sample in humidified H_2 (3% H_2O). Physical characterization of the anode composites were carried out using scanning electron microscopy (SEM) (FEI Quanta 600 ESEM) and X-ray diffraction (XRD) using Cu K_α radiation. BET isotherms were measured using Kr adsorption at 78 K and were used to determine surface areas.

Redox isotherms (i.e., sample composition as a function of pO_2 for the REV_4/YSZ and $REAEV_4$/YSZ composites were measured using a coulometric-titration cell that has been previously described in detail [29]. The cell consisted of a YSZ tube with Ag electrodes painted onto the inner and outer surfaces. Approximately 0.1 g of sample was placed in the cell and then pre-reduced in flowing 10%H_2:90%N_2 at 973 K for 4 h. The cell was then purged with CO and sealed. The H_2 treatment insured that the measurements were started from the reduced state of the sample. Precise amounts of oxygen were added to the cell in a stepwise fashion by pumping oxygen through the YSZ electrolyte by applying a voltage across the two electrodes using a Gamry Instruments potentiostat. After each O_2 addition the sample was allowed to equilibrate (which could take up to two days) and then the pO_2 in the cell was determined from the voltage across the two electrodes via the Nernst equation. The oxygen stoichiometry of the sample was determined from the known starting stoichiometry and the amount of O_2 pumped into the cell. All coulometric titration experiments were performed with the sample at 973 K.

Button-sized cells were used in all fuel cell measurements. These cells were fabricated using porous-dense-porous tri-layer YSZ wafers that were produced using tape casting methods that have been described in detail previously [27]. For each cell, the dense electrolyte layer was 80 μm thick and 1 cm in diameter. The 60% porous YSZ layers on each side of the dense electrolyte layer were 50 μm thick with a BET surface area 0.3 $m^2 g^{-1}$. Sr-doped lanthanum ferrite ($La_{0.8}Sr_{0.2}FeO_3$, LSF) was added to one porous layer to form a cathode using multiple cycles of infiltration of an aqueous solution containing dissolved $La(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%), $Sr(NO_3)_2$ (Alfa Aesar, 99%) and $Fe(NO_3)_3 \cdot 9H_2O$ (Fisher Scientific) in the appropriate molar ratios, followed by calcination in air at 723 K [30–32]. These cycles were repeated until a 40% weight loading of LSF was obtained. After the infiltration steps the composite cathode was calcined to 1123 K for 4 h to form the perovskite structure. The $Ce_{0.7}Sr_{0.3}VO_{3.85}$ anode was synthesized in a similar manner except that a 30 wt% loading was used and it was calcined to only 973 K. After forming the $Ce_{0.7}Sr_{0.3}VO_{3.85}$–YSZ composite anode, it was reduced in humidified H_2 (3% H_2O) at 973 K prior to cell testing. For one cell, 1 wt% Pd was added to the anode side by infiltration with an aqueous solution of $(NH_3)_4Pd(NO_3)_2$.

For fuel cell testing, silver paste was applied to both electrodes and used as the current collector and the cells were mounted onto an alumina tube with a ceramic adhesive (Aremco, Ceramabond 552). All the cell tests were performed with the anode exposed to humidified H_2 (3% H_2O) and the cathode to ambient air. Electrochemical impedance spectra were measured between 0.1 Hz and 300 kHz with a 1 mA AC perturbation, and *V–i* polarization curves were measured using a Gamry Instruments potentiostat.

3. Results

The solubility limits of the alkaline earth dopants in the REV_4 structure were determined by both the appearance of secondary phases as determined by XRD and the concentration at which a discontinuity was observed in plot of the REV_4 lattice parameter versus alkaline earth concentration. For the sake of example, Sr- and Ca-doped $CeVO_4$ will be used to illustrate these methods. The $Ce_{1-x}Sr_xVO_{4-0.5x}$ zircon structure was confirmed by the presence of the expected diffraction peaks near 24.0, 32.4, 34.1, 36.4, 38.9, 43.2, 46.1, and 48.0 degrees 2θ [23, 25]. Fig. 1 shows the 21 to 31 degrees 2θ region of the powder XRD pattern for this material for several *x* values. This region of the spectrum contains

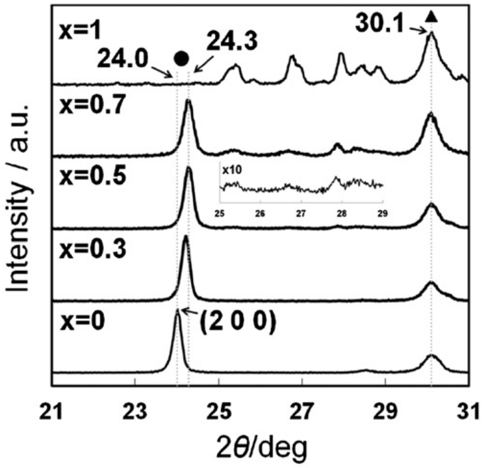

Fig. 1. XRD patterns of $Ce_{1-x}Sr_xVO_{4-0.5x}$–YSZ composites with different Ce:Sr ratios (x=0, 0.3, 0.5, 0.7, 1) that were calcined in air at 973 K. The peaks labeled ● and ▲ correspond to $Ce_{1-x}Sr_xVO_{4-0.5x}$ and ▲, respectively.