STABILITY AND CONDUCTIVITY OF PEROVSKITE OXIDES UNDER ANODIC CONDITIONS

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ABSTRACT

The transition metal perovskites are interesting high temperature electrode materials because of their tendency for mixed ionic and electronic conduction and enhanced catalytic properties. The electrical conductivity and chemical stability of ABO$_3$ (A = La, Sr; B = Ni, V, Ti, Nb, Mo, W) with or without dopants in reducing atmospheres have been examined. Neither the rare earth vanadates, such as LaVO$_3$, nor the alkaline earth vanadates, with the exception of SrVO$_3$, are good electronic conductors. SrVO$_3$ shows excellent electronic conductivity of 1000 S/cm at 800°C and at low oxygen pressures, but is unstable under more oxidizing conditions. However, strontium-doped lanthanum vanadates are stable under fuel inlet conditions with oxygen partial pressures of $10^{-14}$ to $10^{-20}$ atm. La$_{0.5}$Sr$_{0.5}$VO$_3$ has a conductivity of 300 S/cm at 25°C in air and 50 S/cm at 800°C and $P_{O_2} = 10^{-20}$ atm, respectively. These results indicate that vanadium-containing compounds have high temperature electronic conductivity in reducing atmospheres, which is requirement for solid oxide fuel cell anodes.

INTRODUCTION

High temperature solid oxide fuel cells (SOFCs) offer many advantages over traditional energy conversion systems, for example, high efficiency, reliability, modularity, fuel adaptability, and very low levels of NO$_x$ and SO$_x$ emissions (1). In the operation of a fuel cell, oxygen ions are transported from air through the cathode/electrolyte/anode laminate to oxidize the fuel on the other side. Thus, electrode materials with good electronic and ionic conductivities, acting as both current collectors and catalysts, are desired for the SOFC operation to minimize IR losses. In addition to these properties, the electrode materials are required to possess matching thermal expansion and chemical compatibility with the electrolyte.

Lanthanum manganite has been commonly used as the cathode with the YSZ electrolyte due to its high electronic conductivity and chemical compatibility. Nickel cermet has been the usual anode material. However, one of the problems of the nickel-cermet anode when methane is used as fuel is that the nickel metal catalyses the dehydrogenation reaction of methane to form a layer of carbon between the zirconia and...
the nickel, thereby inhibiting the anode reaction and good performance of the SOFC \(2\). Nickel cermets also suffer from thermal mismatch with YSZ, giving rise to stresses and leading to failure. Nickel and LSGM has been found to form an interfacial reaction product with high resistivity. It is therefore necessary to develop new anode materials if methane is to be used directly as fuel and/or if LSGM is to be used as electrolyte in the SOFC. Developing anode materials that will satisfy the requirements simultaneously is a significant challenge. Some of the required properties deteriorate when others are improved, as for example, electronic conductivity versus ionic conductivity or single-phase composition versus stability over a wide range of oxygen partial pressure. To optimize the anode material requires a compromise in the chemical and physical properties.

Oxides have been targeted as potential anode materials because they could simultaneously transport oxygen ions and electrons, thus being less prone to the problem of coking \(3\) as well as less likely to suffer from sulfur poisoning \(4\). In particular, perovskite oxides \(\text{ABO}_3\) have many useful features as alternative anode materials, including increased stability of the mixed valence states of Ti, V, Nb, Mo, W, etc., in the perovskite structure, the mobility of oxygen ions, and the stabilization of noble metal oxides in high dispersion \(5\). The composition \(\text{ABO}_3\) can be varied extensively by atomic substitution or by non-stoichiometry on either cation or anion sublattices. One can vary the interaction between the metal and oxygen orbitals in this structure by substituting the large cation and/or the transition metal ion to obtain a wide variation in properties. Electronic and ionic conductivities, sintering behavior, and catalytic performance are all modified by such substitutions. The combination of an inactive A ion (such as \(\text{La}^{3+}\) or \(\text{Sr}^{2+}\)) with an active B ion (such as \(\text{Co}^{3+}, \text{Mn}^{3+}, \text{Ti}^{3+}, \text{Ru}^{4+}\)) makes a priori choice of the active site reasonable in catalysis \(6\). Moreover, the properties of the B ion and its neighbor oxygen ions can be modified by the choice of the A ion. Specific compositions with optimized properties have been developed for applications in SOFCs and as potential catalysts for environmental applications. Several perovskite oxides have been investigated as alternative anode materials, including \(\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3\delta\) \(7\), \(\text{CaTiO}_3\) doped with Fe \(8\), \(\text{LaCr}_{1-x}\text{Ni}_x\text{O}_3\) \(9\), \(\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3\) \(10\), and \(\text{NdCrO}_3\) doped with Ti \(11\). The requirements of SOFC anodes greatly limit the number of possible candidate materials. Past efforts to develop a single-phase material that exhibits both stability over the oxygen partial pressure range associated with typical anode operation and sufficient electrical conductivity have been unsuccessful.

In this work, mixed perovskites such as \(\text{LaNi}_{1-x}\text{M}_x\text{O}_3\) \((\text{M} = \text{Ti}, \text{V}, \text{Nb}, \text{Mo}, \text{W})\), \(\text{La}_{1-x}\text{Sr}_x\text{VO}_3\delta\) \((x = 0.2, 0.3)\), and \(\text{SrV}_{1-x}\text{Ti}_x\text{O}_2\delta\) \((x = 0, 0.5)\) have been studied. We have attempted to force a change in the oxidation states of the transition metals in order to improve the electrical properties of these materials in the perovskite structure. We have measured electrical conductivity of such oxides over a range of composition, oxygen partial pressure and temperature.

**EXPERIMENTAL**

The specimens for study were prepared by solid state reaction of 99.9% pure oxide powders. \(\text{La}_2\text{O}_3\) and \(\text{SrCO}_3\) were heated beforehand in air to 800 °C and 200 °C, respectively. Stoichiometric amounts of \(\text{La}_2\text{O}_3\), \(\text{NiO}\), \(\text{SrCO}_3\), \(\text{TiO}_2\), \(\text{V}_2\text{O}_5\), \(\text{MoO}_3\), \(\text{WO}_3\),
and Nb$_2$O$_5$ were mixed, ground in methanol for 20 minutes, and cold-pressed to form tablets. The tablets were sintered in air or in controlled atmospheres. The synthesis was carried out with intermediate regrinding. Additional pellets were made for x-ray analysis. The presence of a single phase of the final product was confirmed by x-ray diffraction on a Nicolet 12 automated diffractometer using Cu K$_\alpha$ radiation. X-ray diffraction analysis was also done to check the stability of a sample following the conductivity measurement at low oxygen partial pressure.

The samples for conductivity measurement were 6 mm in diameter and 15 mm long. The conductivity was measured by the four-probe dc method. A constant current of 100 mA was applied by a Keithley 225 current source and the potential drop recorded by an HP 34401A multimeter with input impedance of $10^{10}$ ohms. A gas mixture of carbon monoxide and carbon dioxide, controlled by an MKS mass-flow controller, type 1159B and an MKS readout, type 247C, was used to fix the oxygen partial pressure.

RESULTS AND DISCUSSIONS

Stability

A partial list of perovskite oxides examined is given in Table 1. Their stability and electrical conductivities were studied over an oxygen partial pressure range of $10^{-20}$ - $10^{-14}$ atm at 800°C. Nickel was included in all initial compositions because of its superior catalytic properties. LaNi$_{1-x}$M$_x$O$_3$ can be regarded as a solid solution of LaNiO$_3$ or as a compound containing enough M to ensure charge balance when all nickel is in the Ni$^{2+}$ state. Although LaNiO$_3$ becomes unstable at an oxygen partial pressure of $10^{-2}$ atm and 1000 °C (12), LaNi$_{1-x}$M$_x$O$_3$ mixed perovskites (M = Ti, V, Nb, Mo, W) are stable under anodic conditions. This was confirmed by x-ray diffraction results as shown in Figure 1. No change in the x-ray diffraction pattern was observed after the materials had undergone conductivity measurements under reducing conditions.

| Composition          | Preparation* | Conductivity (S/cm) at 25 °C | Conductivity (S/cm) at 800 °C |
|----------------------|--------------|-----------------------------|-------------------------------|
| LaNi$_{0.67}$Nb$_{0.33}$O$_3$ | 1450 °C, 9hrs | 1.2x$10^{-2}$                | 9.5x$10^{-2}$                 |
| LaNi$_{0.5}$V$_{0.5}$O$_3$    | 1500 °C, 9hrs | 5.4x$10^{-2}$                | 8.2                        |
| LaNi$_{0.5}$Sr$_{0.25}$Ti$_{0.25}$O$_3$ | 1400 °C, 9hrs | 8.4x$10^{-3}$                | 5.8x$10^{-1}$                 |
| LaNi$_{0.75}$Mo$_{0.25}$O$_3$  | 1400 °C, 8hrs | 2.7x$10^{-1}$                | 5.98                        |
| LaNi$_{0.75}$W$_{0.25}$O$_3$   | 1400 °C, 9hrs | 5.4x$10^{-2}$                | 4.8x$10^{-1}$                 |
| SrVO$_3$-δ             | 1400 °C, 6hrs | 3.2x$10^{-1}$                | 1.0x$10^{-3}$                 |
| SrV$_{0.5}$Ti$_{0.5}$O$_3$-δ | 1450 °C, 9hrs | 7.1x$10^{-3}$                | 9.7x$10^{-1}$                 |
| La$_{0.8}$Sr$_{0.2}$VO$_3$-δ | 1450 °C, 9hrs | 1.2x$10^{-2}$                | 4.5x10                        |
| La$_{0.7}$Sr$_{0.3}$VO$_3$-δ | 1450 °C, 9hrs | 3.0x$10^{-6}$                | 1.2x$10^{-2}$                 |
| La$_{0.9}$VO$_3$-δ        | 1450 °C, 9hrs | 3.3                        | 2.9                          |

* LaNi$_{1-x}$M$_x$O$_3$ in air and La$_{1-x}$Sr$_x$VO$_3$-δ in forming gas (H$_2$:Ar = 7:93)

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Subsequent studies focussed on perovskite containing vanadium since SrVO$_3$ is known to be a good electronic conductor in reducing atmosphere. Powder x-ray diffraction patterns for Lai-xSr$_x$VO$_3$ system are shown in Figure 2 with no change before and after conductivity measurement. The stability of LaVO$_3$, as one end member of Lai-xSr$_x$VO$_3$, was determined by TGA to be stable when oxygen partial pressure is

**Figure 1.** Powder x-ray diffraction patterns for (a) LaNi$_{0.67}$Nb$_{0.33}$O$_3$, (b) LaNi$_{0.75}$Mo$_{0.25}$O$_3$ (c) LaNi$_{0.75}$W$_{0.25}$O$_3$, (d) LaNi$_{0.5}$V$_{0.5}$O$_3$, (e) LaNi$_{0.5}$V$_{0.25}$Ti$_{0.25}$O$_3$.

**Figure 2.** Powder x-ray diffraction patterns for (a) La$_0.7$Sr$_0.3$VO$_3$, (b) La$_0.8$Sr$_0.2$VO$_3$, (c) La$_0.6$VO$_3$. 

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less than $10^{-12}$ atm at 1000°C (12). SrVO$_3$ is the other end member of La$_{1-x}$Sr$_x$VO$_3$, could form from the reduction of Sr$_2$V$_2$O$_7$ at 1250°C in forming gas (Ar:H$_2$ = 93:7). This was confirmed by x-ray diffraction analysis as shown in Figure 3 (a). However, SrVO$_3$ is stable only when oxygen partial pressure is less than $10^{-17}$ atm at 800°C according to this work. Second phases appeared when the oxygen partial pressure exceeded this limit. Additional phases shown in Figure 3(d) were also found in doped SrVO$_3$, i.e., Sr$_{0.5}$Ti$_{0.5}$O$_3$ and Sr$_{0.5}$Zr$_{0.5}$O$_3$, when we attempted to stabilize the SrVO$_3$ phase at higher oxygen pressure. The x-ray analysis for oxidized SrVO$_3$ is shown in Figure 3(b). The major peaks correspond to Sr$_3$V$_2$O$_8$, an apatite phase isostructural with Sr$_3$P$_2$O$_8$. Similar results were observed for the Ba-V-O system by Liu and Greedan (13). According to their studies, the phases in oxidized SrVO$_3$ were likely Sr$_3$V$_2$O$_8$ as the major phase and a vanadium-rich minor phase with the formula Sr$_x$VO$_y$ (x < 1). The standard free energies of formation of SrVO$_3$ and Sr$_3$V$_2$O$_8$ per mole of oxygen at 25°C are $-909.1$ kJ and $-897.9$ kJ (14) respectively, indicating Sr$_3$V$_2$O$_8$ is less stable than SrVO$_3$. However, it is possible that a more stable Sr-deficient apatite phase may form from SrVO$_3$, with a composition Sr$_{2+x}$V$_2$O$_{7+x}$ and a corresponding $\Delta G^\circ = -1026$ kJ per mole of oxygen. Meanwhile, SrVO$_3$ has a high conductivity of $3 \times 10^3$ S/cm at 25 °C, but Sr$_3$V$_2$O$_8$ is a insulating compound where the vanadium ions are isolated in tetrahedral coordination.

![Powder x-ray diffraction patterns](image)

**Figure 3.** Powder x-ray diffraction patterns for SrVO$_3$ (a) as-prepared, (b) oxidized after conductivity measurement; and Sr$_{0.5}$Ti$_{0.5}$O$_3$ (c) as-prepared, (d) oxidized after conductivity measurement.

**Electrical Properties**

Four-probe dc conductivity results of dense pellets obtained at 800°C over a range of oxygen partial pressures of $10^{-20} - 10^{-14}$ atm are shown in Figure 4 for the LaNi$_{1-x}$M$_x$O$_3$ (M = Ti, V, Nb, Mo, W) samples. The conductivity of LaNi$_{0.5}$V$_{0.5}$O$_3$ decreased with decreasing oxygen partial pressure, indicating a p-type behavior. Although the predominant oxidation state of vanadium is V$^{4+}$ in LaNi$_{0.5}$V$_{0.5}$O$_3$, prepared in air, some of

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V⁵⁺ might coexist with lanthanum vacancies to ensure the charge balance. The mixed valence state might allow conductivity by transfer of electron holes between V⁴⁺ and V⁵⁺. The decrease of V⁵⁺ concentration with decreasing oxygen partial pressure results in a lower electrical conductivity. This is consistent with the LaNi₀.₅V₀.₂₅Tio.₂₅O₃ system where the replacement of V⁴⁺ by Ti⁴⁺ leads to a decrease of electrical conductivity as shown in Fig. 4, assuming the conductivity contribution from Ti⁴⁺ is negligible. In fact, Ti⁴⁺ in LaNi₀.₅Ti₀.₅O₃ is so stable that LaNi₀.₅Ti₀.₅O₃ is an insulator even under reducing atmospheres. In contrast with the other oxide systems in Fig. 4, the highest electrical conductivity was observed for LaNi₀.₅V₀.₅O₃. In the case of LaNi₁₋ₓMₓO₃ (M = Nb, Mo, W), the electrical conductivity is only a weak function of oxygen partial pressure. A slight p-type behavior is also observed for these oxides. It is suggested that a mixed valence state of Ni³⁺ and Ni²⁺ might dominate the conduction process. The conductivity of LaNi₀.₇₅Mo₀.₂₅O₃ was found to be consistent with previous work (15). The comparison of the electrical conductivities at 25 °C with those at 800 °C in Table 1, show that all of our samples prepared in air are semiconductors. Similarly, we are in accord with the electrical conductivity studies for LaNi₀.₇₅W₀.₂₅O₃ (16).

The variation of electrical conductivity as a function of oxygen partial pressure at 800°C for La₁₋ₓSrₓVO₃₋δ is shown in Figure 5. This system exhibits a composition controlled metal-insulator (M-I) transition in a temperature range of -196°C ~ 527°C (17). The metal-insulator transition occurs at x ≈ 0.2. No conductivity data are available for high temperature or over a range of oxygen partial pressures. Our experimental data show that the conductivity of La₀.₆Sr₀.₄VO₃₋δ and La₀.₇Sr₀.₃VO₃₋δ increased slightly, indicating a weak n-type behavior. However, the incorporation of Sr²⁺ ions onto La³⁺ sites leads to the formation of V⁴⁺ ions in place of V³⁺ which enhance conductivity in the system. Since La₁₋ₓSrₓVO₃₋δ are unstable under more oxidizing conditions, and their

**Figure 4.** The dependence of conductivity on oxygen pressure at 800 °C for: (a) LaNi₀.₆₇Nb₀.₃₃O₃ (also shown in inset), (b) LaNi₀.₅V₀.₂₅Ti₀.₂₅O₃, (c) LaNi₀.₅V₀.₅O₃, (d) LaNi₀.₇₅W₀.₂₅O₃, (e) LaNi₀.₇₅Mo₀.₂₅O₃.
electrical conductivities are not strongly dependent on oxygen partial pressure, the variation of conductivity of La_{0.8}Sr_{0.2}VO_{3-δ} and La_{0.7}Sr_{0.3}VO_{3-δ} with temperature were measured in forming gas (Ar:H_{2} = 93:7, P_{O2} = 10^{-19} \text{ atm at 800°C}) as shown in Figure 6. The plots of conductivity versus temperature show a linear decrease with increasing temperature, consistent with metallic behavior. This result is in agreement with Dougier’s previous study (17).

Figure 5. The dependence of conductivity on oxygen pressure at 800 °C: (a) La_{0.7}Sr_{0.3}VO_{3-δ}, (b) La_{0.8}Sr_{0.2}VO_{3-δ}, (c) La_{0.9}VO_{3-δ}.

Figure 6. Variation of conductivity versus temperature in forming gas (H_{2} : Ar = 7 : 93) (a) La_{0.7}Sr_{0.3}VO_{3-δ}, (b) La_{0.8}Sr_{0.2}VO_{3-δ}.
CONCLUSIONS

Electrical conductivities for the perovskite oxides LaNi_{1-x}M_{x}O_{3} (M = Ti, V, Nb, Mo, W) were found not to exceed 1 S/cm at P_{02} = 10^{-20} atm and 800°C. All of these oxides are stable over a wide oxygen partial pressure range (10^{-20} – 1 atm), and are p-type semiconductors. In contrast with these oxides, La_{1-x}Sr_{x}VO_{3-d} (x = 0.2, 0.3) shows metallic behavior with high electrical conductivities up to 120 S/cm at P_{02} = 10^{-20} atm and 800°C. Strontium doped LaVO_{3} is stable under SOFC fuel inlet conditions. High electrical conductivity and relatively good stability indicate that La_{1-x}Sr_{x}VO_{3-d} system oxide are promising anode materials.

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