



## Nafion-Bimevox Composite Membrane for Fuel Cell Applications

Richard Lawson,<sup>a,c</sup> Chunsheng Wang,<sup>a,\*</sup> Jian Hong,<sup>a,\*\*</sup> Jianxin Ma,<sup>a</sup>  
Bin Fang,<sup>a</sup> and Deryn Chu<sup>b,\*</sup>

<sup>a</sup>Department of Chemical Engineering/Center for Manufacturing Research, Tennessee Technological University, Cookeville, Tennessee 38505, USA

<sup>b</sup>U.S. Army Research Laboratory, Sensors and Electronic Devices Directorate, Adelphi, Maryland 20783-1197, USA

To suppress methanol crossover in direct methanol fuel cells (DMFCs), a Nafion-Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> composite membrane was prepared by recast method. Oxygen-ion conductive Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> powders were highly dispersed in a Nafion 117 membrane to physically block methanol crossover and/or chemically oxidize the methanol, which was confirmed by the difference in the methanol diffusion coefficient between recast Nafion and Nafion-Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> composite membranes. Interestingly, mixing 20 wt % Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> into Nafion 117 membrane largely suppressed the methanol crossover, but only slightly decreased the proton conductivity of the membrane, resulting in a large improvement in the DMFC performance. The stabilities of Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> in 5% Nafion solution, water, and 1 M H<sub>2</sub>SO<sub>4</sub> were measured using an inductively coupled plasma atomic emission spectrometer, and the electrochemical stability of Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution was obtained using cyclic voltammetry. The oxygen-ion conductivities of Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> at temperature ranges from 80 to 400°C were also measured. © 2006 The Electrochemical Society. [DOI: 10.1149/1.2372699] All rights reserved.

Manuscript submitted January 20, 2006; revised manuscript received August 2, 2006. Available electronically November 15, 2006.

Direct methanol fuel cells (DMFCs) have advantages over other fuel cells because they use a liquid fuel which can be easily stored and transported instead of a gas. Unfortunately, DMFC have much lower power densities than hydrogen fed polymer electrolyte membrane fuel cells (PEMFC) due to methanol crossover and carbon monoxide poisoning of the platinum catalysts. Methanol crossover causes significant reduction of both the cathode potential and of the fuel utilization due to a chemical short-circuit reaction of crossed over CH<sub>3</sub>OH with O<sub>2</sub> at the cathode.

Methanol crossover can be physically reduced by using thicker membranes, inserting a metallic barrier (Pd) into Nafion,<sup>1,2</sup> or mixing the membrane with other polymers,<sup>3</sup> ceramics,<sup>4,6</sup> or zeolites.<sup>7</sup> All of these methods reduced methanol crossover but increased the cell resistance, resulting in a lower performance, even more so than due to the crossover itself. Another way to reduce the methanol crossover is to chemically oxidize methanol with O<sub>2</sub> in the Nafion layer by dispersing nano-Pt particles in a Nafion membrane.<sup>8</sup> Because the PEM is a strong acid, it is conceivable that CO<sub>2</sub> produced as a result of methanol oxidation in the Pt-PEM is not present in the ionized form, and will be exhausted through the hydrophobic backbone to the anode and the cathode.<sup>8</sup> A direct methanol fuel cell, composed of Pt-Ru anode/Pt-PEM/Pt cathode with catalysts loading of 2 mg/cm<sup>2</sup> and fed with 1 M CH<sub>3</sub>OH and humidified O<sub>2</sub> at 90°C, showed 200 mA/cm<sup>2</sup> at 0.36 V.<sup>8</sup> Because Pt is a good electronic conductor, the amount and distribution of Pt in Nafion should be carefully controlled to prevent the short circuit of the Nafion electrolyte. If the Pt in the Nafion can be replaced by electronic insulators, which have high catalytic activity for the oxidation of methanol, it will greatly simplify the membrane processing procedure and decrease the cost.

Bi<sub>4</sub>V<sub>2(1-x)</sub>Me<sub>2x</sub>O<sub>(11-x)</sub> (abbreviated as BIMEVOX), formed by partial substitution of V with metal in Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>, has a very low electronic conductivity but is a very good catalyst for the oxidation of propane in the temperature range 300–700°C.<sup>9,10</sup> BISBVOX has the highest reported low-temperature oxygen-ion conductivity of ~10<sup>-2</sup> S/cm at 315°C.<sup>11</sup> Because oxidation of methanol is easier than propane, the BISBVOX in Nafion should also be a good catalyst for the chemical oxidation of methanol. Therefore, BISBVOX

may be a good candidate for reducing the methanol crossover if it can be highly dispersed in a Nafion membrane. In a BISBVOX-Nafion composite membrane, BISBVOX not only can physically decrease methanol crossover in the same way that insertion of other ceramics has shown, but also may chemically oxidize the methanol in the Nafion membrane to reduce the methanol crossover. The oxygen vacancies created by the catalytic oxidation of methanol will be refilled by the migration of oxygen<sup>9,10</sup> in the Nafion. Another potential advantage of using a BISBVOX-Nafion composite membrane is that the oxygen-ion conducting particles exposed on the surface of the composite membrane may also reduce CO poisoning of the Pt catalyst by oxidizing CO to CO<sub>2</sub>. It was reported that the oxide-ion conductor CeZrO<sub>2</sub> supported Pt electrocatalyst exhibits 78% CO conversion and 96% CO<sub>2</sub> selectivity at 60°C in the presence of oxygen in H<sub>2</sub> + CO fuel.<sup>12</sup> A synergistic redox model for metal-CeO<sub>2</sub> has been proposed, in which the metal particle participate provides adsorption sites for CO, while the ceria supplies the required oxygen ions. The nano-Au (or Pt) increases the amount of surface oxygen in ceria. This increase can occur through partial lattice filling of vacant Ce sites with Au<sup>δ+</sup>, which would create additional oxygen vacancies on the surface of the Ce<sup>4+</sup>-O<sub>2</sub> fluorite-type oxide.<sup>13</sup>

In this paper, an oxygen-ion conducting Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> was dispersed in Nafion polymer to form a Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub>-Nafion composite membrane. The methanol crossover and performance of a direct methanol fuel cell with a Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub>-Nafion composite membrane was investigated.

### Experimental

**Ceramic preparation and characterization.**—Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> was synthesized by mixing stoichiometric amounts of bismuth oxide, vanadium oxide, and antimony oxide (Sigma-Aldrich) by mechanical ballmilling for 6 h with ethanol. Fully mixed and dried powder was placed into an alumina crucible and heated at 650°C for 24 h. Reacted powders were then mechanically ballmilled for 3 h to decrease particle size before any further use. The composition, phase, and purity of Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> were verified by powder X-ray diffraction (XRD) using a Bruker-AXS D8 powder high resolution parallel beam X-ray diffractometer with Cu X-ray source.

Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> disk pellets for conductivity measurements were made by isostatically pressing powders to a pressure of 3 metric tons for 2 min and sintered at 800°C for 1 h or at 810°C for 10 h in an alumina crucible. Connections to the pellets were made using silver wire that was attached with silver paste. Conductivity mea-

\* Electrochemical Society Active Member.

\*\* Electrochemical Society Student Member.

<sup>c</sup> Present address: School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA.

<sup>z</sup> E-mail: cswang@ntech.edu

surements were made with four electrode ac impedance spectroscopy in temperatures ranging from 80 to 400°C using a Solartron 1287A potentiostat and a Solartron 1250 frequency response analyzer with frequency range from 1 MHz to 0.1 Hz at a potentiostatic signal amplitude of 100 mV. The oxygen-ion conductivity and electronic conductivity were calculated from the impedances at high-frequency and low frequency, respectively.

*Chemical and electrochemical stabilities of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in simulated fuel cell environments.*— The chemical stabilities of the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  ceramic in 1 M  $\text{H}_2\text{SO}_4$  solution, in water, and in 5% Nafion solution were determined by measuring the amount of constituent metal ions present in the solutions after storage in the solution for 3 months using the inductively coupled plasma atomic emission spectrometer (ICP). ICP was performed using a Perkin-Elmer Optima 3000 XL simultaneous ICP spectrometer. The electrochemical stability of the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in 1 M  $\text{H}_2\text{SO}_4$  solution (a simulated fuel cell environment) was investigated using cyclic voltammetry (CV) at 25°C with a scan rate of 10 mV/s. The  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  electrode was fabricated as follows: 10 mg of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  catalyst was mixed with 5 mg of carbon black, 0.25 mL of 5 wt % Nafion solution (Alfa Aesar), and 1 mL of ethanol. The mixture was ultrasonicated for 30 min and then 10  $\mu\text{L}$  was pipetted out of the resulting suspension on to a glassy carbon substrate (3 mm diam). A mercury/mercury sulfate electrode (0.68 V vs the normal hydrogen electrode (NHE)), and a platinum wire were used as the reference electrode and the counter electrode, respectively. A 1 M  $\text{H}_2\text{SO}_4$  solution was used as the electrolyte. Before each measurement, the solution was purged with high-purity nitrogen for 30 min to remove the oxygen. For comparison, cyclic voltammetry of carbon black in 1 M  $\text{H}_2\text{SO}_4$  was also tested.

*Catalytic activity of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  for methanol oxidation.*— The catalytic activity of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  for chemical oxidation of methanol in a composite membrane DMFC was indirectly evaluated by testing its electrocatalytic activity in 1 M  $\text{H}_2\text{SO}_4$  + 3 MCH<sub>3</sub>OH solution using the linear sweep voltammetry (LSV) technique in the potential range of 0–1.1 V at a scan rate of 10 mV/s. The  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  used for electrocatalytic activity testing was heat-treated at 650°C for 3 h under Ar + H<sub>2</sub> atmosphere to turn it from an oxygen-ion conductor/electron insulator to mixed oxygen-ion/electron conductor. The catalytic activity of Pt for methanol oxidation in 1 M  $\text{H}_2\text{SO}_4$  + 3 MCH<sub>3</sub>OH solution was also tested for comparison.

*Preparation and characterization of Nafion-20%  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  composite membrane.*— The  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  powders used for the composite membrane were sieved using a mesh screen to obtain very fine ceramic particles. The Nafion-20%  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  composite membrane was fabricated by mixing the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  into Nafion 117 solutions, followed by agitation in an ultrasonic mixing bath for 15–30 min. The evenly distributed mixture was placed in a 40°C oven overnight until the solution evaporated, leaving a solid polymer/ceramic membrane. Nafion solution was also brushed onto both sides of the composite after they had dried. After the membranes had completely dried, they were hot pressed at 135°C and 400 psi until they reached a consistent thickness. Two pure Nafion (recast Nafion and Nafion 117) membranes were used to compare to the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ -Nafion composite membranes. The recast Nafion membrane was made from a 5 wt % of Nafion 117 solution (BioChemika, Fluka) using the same method for the composite membrane. Commercial Nafion 117 was bought in sheet form from DuPont (DuPont de Nemours and Company, Wilmington, DE).

Proton conductivities of the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ -Nafion composite membranes were measured using a galvanostatic four-point-probe electrochemical impedance spectroscopy (EIS).<sup>14</sup> EIS were measured in deionized water at 80°C from 1 MHz to 0.1 Hz at 10 mV potentiostatic signal amplitude using a Solartron 1287A electrochemical interface and a Solartron 1250 frequency response ana-

Table I. Catalyst loadings of DMFCs.

| Membranes in DMFC  | Thickness (cm) | Anode PtRu loading (mg/cm <sup>2</sup> ) | Cathode Pt loading (mg/cm <sup>2</sup> ) |
|--------------------|----------------|--|--|
| Nafion 117         | 0.018          | 1.80                                     | 0.4                                      |
| Recast Nafion 117  | 0.018          | 1.80                                     | 0.4                                      |
| Composite Membrane | 0.015          | 1.80                                     | 0.4                                      |

lyzer. A four-point-probe cell with two platinum foil outer current-carrying electrodes and two platinum wire inner potential-sensing electrodes was mounted on a poly(tetrafluoroethylene) (PTFE) plate. Membrane samples were cut into strips that were approximately 1.0 cm wide, 5 cm long, and 0.015–0.02 cm thick prior to mounting in the cell. With this method, a fixed ac current was passed between two outer electrodes, and the conductance of the material was calculated from the ac potential difference observed between the two inner electrodes. The method is relatively insensitive to the contact impedance at the current-carrying electrode and is therefore well suited for measuring proton conductivities.

*Electrode and fuel cell operation.*— The cathodes and anodes were made using the method outlined in Ref. 15. In-house gas diffusion electrodes (GDEs) were fabricated using electrocatalyst-Nafion ink painted on a gas diffusion layer to produce the active layer (AL) without chemical transformation of Nafion. PtRu (50:50 atom %) nanocrystallites supported on Vulcan XC-72 conducting furnace black (E-TEK Inc., Somerset, NJ) with 40 wt % loading were used as AL electrocatalysts. Shawinigan acetylene black (Chevron-Texaco, Houston, TX) containing 10% wt % Nafion for the anode and 33% PTFE solution for the cathode was spread as a thin (3 mg cm<sup>-2</sup>) gas diffusion layer (GDL) on Textron (Wilmington, MA) CPW-003 lightweight carbon cloth. The PtRu loading for the anode was 1.8 mg cm<sup>-2</sup>, and 0.4 mg cm<sup>-2</sup> for the corresponding cathodes. Table I shows the catalyst loading at each electrode for each of the membranes tested. Membrane electrode assemblies (MEAs) were prepared by hot-pressing the anode and cathode GDE structures symmetrically on both sides of one Nafion or  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ -Nafion composite membrane between two 125  $\mu\text{m}$  PTFE sheets (McMaster-Carr, Atlanta, GA) at 70 kg/cm<sup>2</sup> for 5 min at 135°C. Before pressing the MEA, the surface was impregnated with ca. 0.3 mg cm<sup>-2</sup> ionomer by brushing with 5 wt % Nafion solution. The active area of all MEAs was 1.0 cm<sup>2</sup>, each of which was punched from a 50 cm<sup>2</sup> piece of MEA.

Considering the fuel energy and fuel crossover, a low anode methanol concentration of 1–2 M is typically needed to achieve the maximum power density of an active DMFC.<sup>16,17</sup> Because both the methanol crossover and fuel energy will be enhanced by the increases of methanol concentration in the anode, it is expected that the difference in performance between conventional Nafion fuel cell and the composite membrane fuel cell will be enlarged at higher concentrations of methanol. Therefore, a high concentration (3 M) of methanol fuel was gravity fed at a rate of 6–7 mL/min at ambient temperature and pure, humidified oxygen at 50°C at a rate of 0.11 L/min. The methanol leaving the cell was caught in a beaker and poured back into the feed container by hand. Another reason for using 3 M methanol fuel is that optimal methanol solution appeared at 3.0–4.0 M in passive DMFCs,<sup>18</sup> in which external pumps or other ancillary devices for fuel and oxidant supply are removed. Potential-current density parameters of DMFCs were obtained using linear sweep voltammetry (LSV) at a scan rate of 1.0 mV s<sup>-1</sup> at 50°C cell temperature.

*Methanol crossover measurements.*— Before methanol crossover measurement, the cells were activated by repeating operation with a rest at open-circuit potential for 1 h, followed by condition-

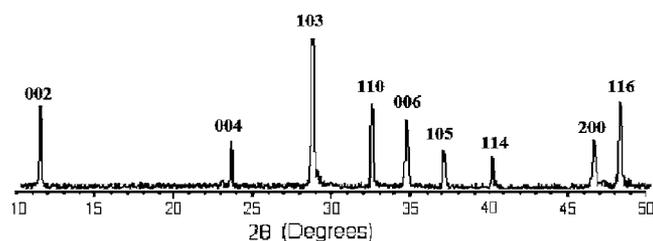


Figure 1. XRD pattern for  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ .

ing at 0.4 V for 30 min and 0.2 V for another 30 min until a steady current was achieved. The limiting crossover currents of membranes were obtained by measuring the steady-state limiting current density ( $J_{\text{lim}}$ ) resulting from complete electro-oxidation at the Nafion membrane/Pt catalyst interface on the cathode side where the humidified oxygen was replaced by well-humidified  $\text{N}_2$  or pure water.<sup>16</sup> The methanol crossover diffusion coefficient was calculated based on the limiting crossover current density.<sup>16</sup>

### Results and Discussion

*$\text{Bi}_2\text{V}_{0.85}\text{Sb}_{0.15}\text{O}_{5.4}$  oxygen-ion conductivity and stability.*— Figure 1 shows the XRD pattern of  $\text{Bi}_2\text{V}_{0.85}\text{Sb}_{0.15}\text{O}_{5.4}$ . The XRD patterns are in agreement with the previously reported XRD data of a ceramic with the same composition.<sup>11</sup> Therefore, the  $\gamma$  phase was correctly synthesized with good purity.

Figure 2 is an Arrhenius plot of ionic conductivity for the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  measured in flowing air. The ionic conductivity of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  is slightly lower but its activation energy (0.72 eV) is slightly higher than that (0.57 eV) reported by Joubert,<sup>11</sup> which may be attributed to a low density of the sintered pellets. Figure 3a shows the scanning electron micrograph (SEM) of the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  pellet cross-section formed by snapping the sintered pellet into half. The image in Fig. 3a shows the high porosity of sintered  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ . A denser pellet was obtained by sintering the pellet at a high temperature (810°C) for a long time (10 h) as shown in Fig. 3b. The oxygen-ion conductivity of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  pellet with a high density is under investigation.

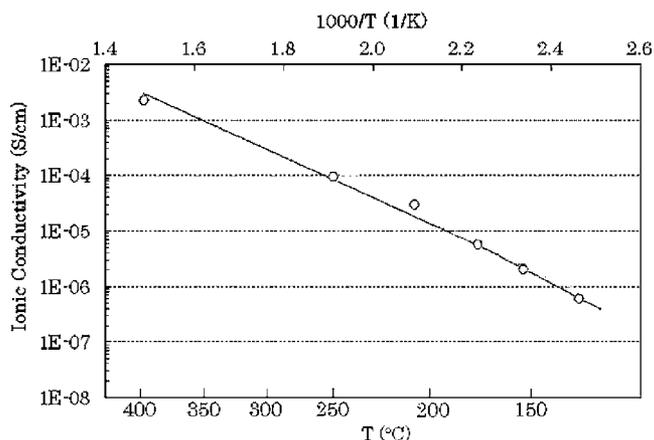


Figure 2. Arrhenius plot of oxygen-ion conductivity for  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ .

The very low electronic conductivity ( $10^{-12}$  s/cm) of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  at room temperature demonstrated that synthesized oxygen-ion conductive  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  is an electronic insulator.

The chemical stabilities of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in water, 5% Nafion solution, and 1 M  $\text{H}_2\text{SO}_4$  solution was also tested by measuring the amount of constituent metal ions present in the solutions after storage in the solution for 3 months. The concentrations of Bi, V, and Sb in the above three liquids were less than 1.6 mg/L, indicating the insolubility of the ceramic in the solutions.

Figure 4 shows the electrochemical stability of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in a 1 M  $\text{H}_2\text{SO}_4$  solution measured using CV at a scan rate of 10 mV/s. The carbon black alone acts like a blank with which to compare the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ . The current at potentials above 1.5 V is due to the oxidation of carbon in the 1 M sulfuric acid medium. Because the current of carbon black in an acid solution is very low, carbon black has been widely used in DMFC as catalyst supporters, although it is thermodynamically unstable at high potentials.  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  shows an oxidation and a reduction peak current below 0.3 V, which is similar to the CV behavior

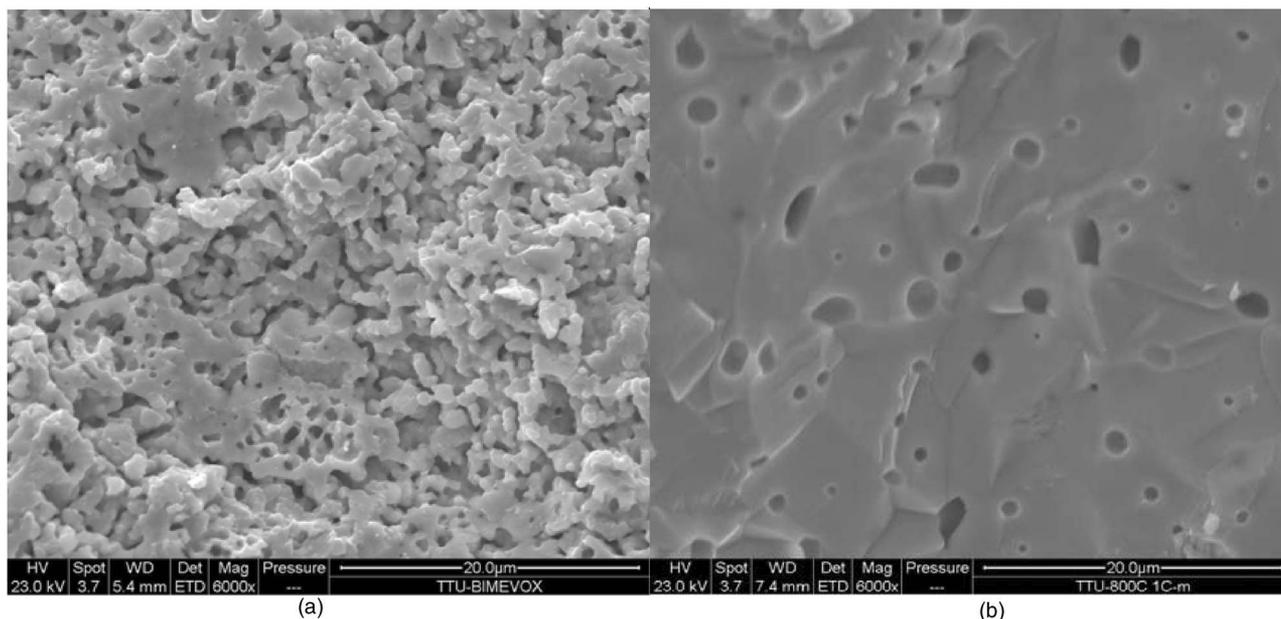
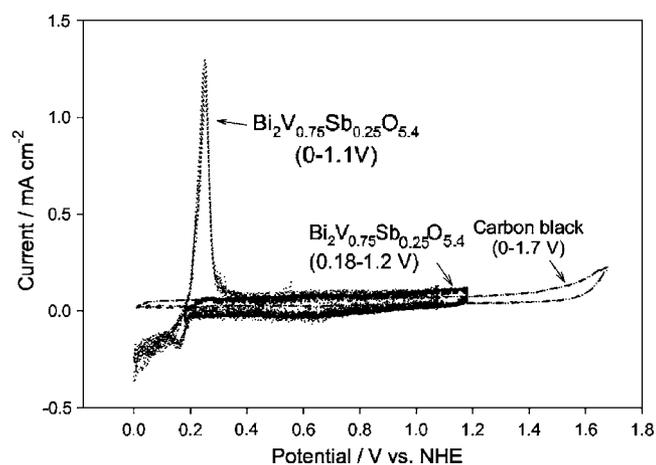


Figure 3. SEM images of sintered  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  pellet cross section used for conductivity measurement. (a) Sintered at 800°C for 1 h, (b) sintered at 810°C for 10 h.



**Figure 4.** CV for  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  and carbon electrodes in 1 M  $\text{H}_2\text{SO}_4$  solution.

of  $\text{WO}_3$  in the same solution (1 M  $\text{H}_2\text{SO}_4$ ).<sup>19</sup> The anodic peak current at 0.25 V is associated with the cathodic peak current at around 0 V because both peak currents disappear when the potentials were scanned from 1.2 to 0.18 V (Fig. 4). The nature of the reversible oxidation and reduction peaks is not clear now. Ganesan et al.<sup>19</sup> attributed the cathodic and anodic peaks of  $\text{WO}_3$  at a potential around 0–0.2 V to hydrogen absorption and desorption in  $\text{WO}_3$ , respectively.  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  may also experience hydrogen absorption and desorption at a low potential because the oxygen-ion conductive perovskite-type oxides such as  $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\delta}$  ( $\text{M} = \text{Y}, \text{Nd}, \text{Yb}$ ) and  $\text{SrCe}_{0.95}\text{M}_{0.05}\text{O}_{3-\delta}$  ( $\text{M} = \text{Yb}, \text{Tm}, \text{Pr}, \text{Tb}$ ) can reversibly absorb/desorb hydrogen in the alkaline solution at room temperature<sup>20</sup> by forming protonic defects through dissociative absorption of water. To form protonic defects, water from the solution dissociates into a hydroxide ion and a proton; the hydroxide ion fills an oxygen-ion vacancy of  $\text{ABO}_3$  oxide, and the proton forms a covalent bond with a lattice oxygen. Whatever the reaction nature is, there is no decrease in peak current even after 50 cycles (5 cycles shown in Fig. 4). Therefore  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  is stable and does not undergo any dissolution in acid medium.

The mixed conductive  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  showed a lower onset catalysis potential (0.3 V vs NHE) for methanol oxidation in 1 M  $\text{H}_2\text{SO}_4 + 3 \text{MCH}_3\text{OH}$  solution than that (around 0.5 V) of Pt in the same solution although the peak current of the former is 10 times less than that of the latter. The low onset oxidation potential of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  is beneficial for effective oxidation of the methanol near the anode side. The low catalytic activity for methanol oxidation may be overcome by increased concentration of the  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in Nafion.

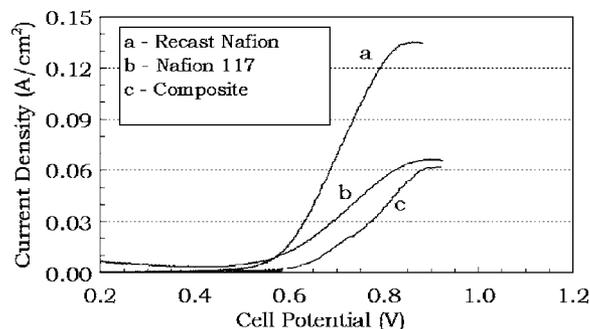
**$\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$ -Nafion composite membrane characterization.**— Figure 5 shows a Nafion-20%  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  composite membrane prepared using the recast method. The  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  particles with yellow color are finely dispersed into the Nafion membrane. Conductivities of recast membranes with and without 20%  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  addition measured in deionized water at 80°C were almost the same (0.24 S/cm), and were higher than commercial Nafion 117 (0.1 S/cm). Normally, the addition of an inactive ceramic such as  $\text{SiO}_2$  into Nafion largely decreases the proton conductivity of Nafion.<sup>5</sup> However, mixing 20% of an oxygen-ion conductive  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  into Nafion retains the proton conductivity of the recast pure Nafion, which indicates that the interfacial layers between oxygen-ion conductor  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  and proton conductor Nafion may accelerate the proton migration because the oxygen-ion conductivity ( $< 10^{-7}$  S/cm) of  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  at room temperature is much lower than the proton conductivity ( $10^{-1}$  S/cm) of Nafion. The detailed mechanism is not yet clear. It



**Figure 5.** (Color online) Photograph of Nafion-20%  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  composite membrane prepared using recast method.

may be attributed to the “composite effect.” In conventional composite materials, a significant conductivity enhancement, the so-called composite effect, usually occurs for a component having a moderate ionic conductivity with another nonconducting component. The conductivity enhancement has been suggested to be due to high conductivity in the interfacial layers between the conducting and insulating phase, and has been observed in almost all of the oxygen-ion based proton co-ion conducting composites (such as  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}\text{-Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ ,  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}\text{-NaOH}$ ,  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}\text{-LiCl}$ ,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\text{Li}_2\text{CO}_3\text{-NaCO}_3$ ,  $\text{BaCe}_{0.8}\text{Y}_{0.15}\text{O}_{2.9}\text{-Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ ,  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}\text{-Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  composites) exhibit a strong composite effect.<sup>21-24</sup>

**Fuel cell performance and characterization.**— Figure 6 is a typical voltammetric curve of the methanol crossover cell described in the experimental section. The high limiting current represents the large methanol crossover rate. The methanol crossover depends on both the methanol diffusion coefficient in the membrane and the membrane thickness. Although the thicknesses of the composite membrane is smaller than the commercial and recast Nafion 117, the composite membrane still had the lowest limiting current, which indicated that  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in the Nafion membrane physically and/or chemically blocked some methanol crossover. However,  $\text{Bi}_2\text{V}_{0.75}\text{Sb}_{0.25}\text{O}_{5.4}$  in a Nafion membrane did not block the proton transportation as indicated by the same proton conductivity (0.24 S/cm). The higher diffusivity of methanol in recast Nafion 117 as opposed to commercial Nafion 117 is due to the low density



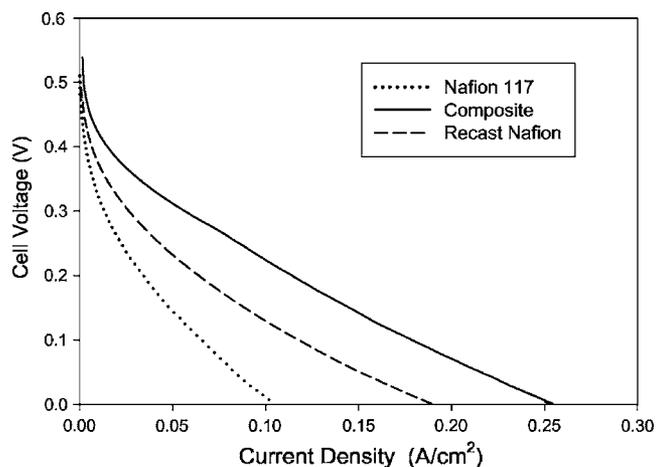
**Figure 6.** Voltammetric curve of methanol crossover for Nafion 117, recast, and composite membranes.

**Table II. Methanol crossover transport parameters for 3 M methanol at 50°C.**

| Membrane           | Diffusion Coefficient (cm <sup>2</sup> /s) | Limiting Crossover Current Density (A/cm <sup>2</sup> ) | Membrane Thickness (mm) |
|--------------------|--|---|-------------------------|
| Nafion 117         | $9.25 \times 10^{-7}$                      | 0.066   | 0.18                    |
| Recast Nafion      | $1.94 \times 10^{-6}$                      | 0.135   | 0.18                    |
| Composite membrane | $7.43 \times 10^{-7}$                      | 0.062   | 0.15                    |

of recast Nafion, which accelerates the transportation of both methanol and protons. To get a qualitative comparison of the amount of methanol crossover in the membranes with different thicknesses, the diffusion coefficients for methanol crossover were calculated based on the limiting current density of each membrane,<sup>16</sup> and shown in Table II. As indicated by the limiting current in Fig. 6, the composite membrane has the lowest crossover diffusion coefficient. Because the composite membrane has the lowest methanol diffusion coefficient and similar proton conductivity to recast and commercial Nafion 117, the composite membrane fuel cell should have better performance than that of recast and commercial Nafion 117 fuel cells.

Figure 7 is the polarization curve for a DMFC at 50°C using composite, recast, and commercial Nafion 117 membranes. As expected from the crossover and proton conductivity measurements, the composite membrane DMFC shows the best performance, followed by the recast membrane fuel cell, and the commercial Nafion 117 fuel cell is the worst. Although the recast Nafion has a higher methanol crossover than that of commercial Nafion 117, the former outperforms the latter because of increased proton conductivity of the recast membrane. A Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub>-Nafion composite membrane developed here may combine both the advantage of the Pt-Nafion membrane in chemical oxidation of methanol and normal ceramic-Nafion membrane in physically blocking the methanol

**Figure 7.** Polarization curves of the DMFCs at 50°C using 3 M methanol solution.

crossover. Moreover, Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> is an oxygen-ion conductor and electronic insulator, which will help the methanol oxidation and prevent the electronic short-circuit of the Nafion membrane. Interestingly, the oxygen-ion addition into Nafion did not decrease the proton conductivity of Nafion. Therefore the oxygen-ion and proton co-ionic conducting membrane may be the next generation membrane for DMFCs. Further fundamental research is still needed to investigate the potential combination reaction between oxygen-ions and protons in Nafion.

### Conclusions

Oxygen-ion conductive Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> is an electronic insulator. It is chemically and electrochemically stable in the 1 M H<sub>2</sub>SO<sub>4</sub> acid solution (a simulate DMFC environment). The addition of Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> ceramic into Nafion membranes greatly reduced methanol crossover with almost no influence on the proton conductivity, resulting in an outstanding performance for DMFCs. The reduced methanol crossover in Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub>-Nafion composite membrane is probably attributable to the combination of physical blocking by ceramic particles and chemical oxidizing the methanol on the Bi<sub>2</sub>V<sub>0.75</sub>Sb<sub>0.25</sub>O<sub>5.4</sub> catalysts. Oxygen-ion and proton co-ionic composite membranes may be a next generation of electrolyte membrane for DMFCs.

### Acknowledgment

This work was partly supported by a Faculty Research Initiation Grant provided by Tennessee Technological University.

Tennessee Technological University assisted in meeting the publication costs of this article.

### References

- J. H. Shim, S. M. Song, W. K. Her, I. G. Koo, and W. M. Lee, *J. Electrochem. Soc.*, **150**, A1583 (2003).
- W. C. Choi, J. D. Kim, and S. I. Woo, *J. Power Sources*, **96**, 411 (2001).
- N. Jia, M. C. Lefebvre, J. Halfyard, Z. Qi, and P. Pickup, *Electrochem. Solid-State Lett.*, **3**, 529 (2000).
- P. Staiti, A. S. Arico, V. Baglio, F. Lufrano, E. Passalacqua, and V. Antonucci, *Solid State Ionics*, **145**, 101 (2000).
- N. Miyake, J. S. Wainright, and E. F. Savinell, *J. Electrochem. Soc.*, **148**, A898 (2001).
- C. Yang, S. Srinivasan, A. S. Arico, and P. V. Baglio, *Electrochem. Solid-State Lett.*, **4**, A31 (2001).
- V. Tricoli and F. Nannetti, *Electrochim. Acta*, **48**, 2625 (2003).
- H. Uchida, Y. Mizuno, and M. Watannabe, *J. Electrochem. Soc.*, **149**, A682 (2002).
- A. Chetouani, B. Taouk, E. B. Richard, E. A. Aad, and A. Aboukais, *Appl. Catal., A*, **252**, 269 (2003).
- A. Chetouani, B. Taouk, and E. B. Richard, *Catal. Today*, **91**, 73 (2004).
- O. Joubert, A. Jouanneaux, M. Ganne, R. N. Vannier, and G. Mairese, *Solid State Ionics*, **73**, 309 (1994).
- H. Roh, H. S. Potdar, K. W. Jun, S. Y. Han, and J. W. Kim, *Catal. Lett.*, **93**, 203 (2004).
- Q. Fu, H. Satsburg, and M. F. Stephanopoulos, *Science*, **935**, 301 (2003).
- M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, **25**, 1463 (2000).
- C. Wang and A. J. Appleby, *J. Electrochem. Soc.*, **150**, A493 (2003).
- X. Ren, T. E. Springer, T. Zawodzinski, and S. Gottesfeld, *J. Electrochem. Soc.*, **147**, 466 (2000).
- K. Scott, W. M. Taama, and P. Argyropoulos, *J. Power Sources*, **79**, 43 (1999).
- J. Han and E. S. Park, *J. Power Sources*, **112**, 477 (2004).
- R. Gangesan and J. S. Lee, *J. Power Sources*, **157**, 217 (2006).
- T. Esaka, H. Sakaguchi, and S. Kobayashi, *Solid State Ionics*, **166**, 351 (2004).
- T. Schober, *Electrochem. Solid-State Lett.*, **8**, A199 (2005).
- B. Zhu, *J. Power Sources*, **114**, 1 (2003).
- B. Zhu, X. Liu, and T. Schober, *Electrochem. Commun.*, **6**, 378 (2004).
- J. Huang, Z. Mao, L. Yang, and R. Peng, *Electrochem. Solid-State Lett.*, **8**, A437 (2005).