

Short communication

Effect of oxygen storage materials on the performance of proton-exchange membrane fuel cells

Zhiqiang Xu, Zhigang Qi^{*}, Arthur Kaufman

H Power Corporation, 60 Montgomery Street, Belleville, NJ 07109, USA

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Abstract

Oxygen storage materials with a chemical composition of $Ce_{0.8}Zr_{0.2}O_2$ and V_2O_5 , were prepared and incorporated into the cathode catalyst layer of proton-exchange membrane fuel cells, respectively. The presence of $Ce_{0.8}Zr_{0.2}O_2$ slightly enhanced the performance of the fuel cell, but the incorporation of V_2O_5 largely decreased the fuel cell performance.

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1. Introduction

A proton-exchange membrane fuel cell will have the highest performance when the reactants are pure hydrogen and oxygen. In reality, air instead of pure oxygen is used as the cathode oxidant because it is readily available from the atmosphere, and it avoids the expense of bottled oxygen.

However, a fuel cell will have lower performance using air than using pure oxygen. First, there is only about 21 vol.% oxygen in air, with the other 79 vol.% being mainly nitrogen. Without considering the presence of water vapor in air for humidification purposes, the partial pressure of oxygen at atmospheric pressure is therefore about 0.21. This lower oxygen partial pressure will result in a cathode voltage loss for several tens of millivolts [1].

Second, in typical operation, the decline is normally much larger, especially at relatively high current densities. This is due to the formation of the so-called “nitrogen blanket”. When oxygen reacts within the catalyst layer, most of inert nitrogen remains in the catalyst layer. The stagnant nitrogen behaves like a blanket to obstruct the diffusion of incoming oxygen to reach the catalyst sites. The result is that the oxygen partial pressure is reduced far below 0.21 at the surface of the catalyst.

A class of ceria-based materials has been widely used in cleaning automotive exhaust [2–8]. These materials have

been found to have fairly high oxygen storage capacity. This allows one to enlarge the operating air-to-fuel window and to achieve the highest conversion efficiency while keeping the oxidant-to-reactant ratio close to the stoichiometric level. Traditionally, high surface area CeO_2 has been used for this purpose. Recently, ZrO_2 has been inserted into the CeO_2 lattice to form a CeO_2 – ZrO_2 solid solution, which increases both the thermal stability and the oxygen storage capacity.

It seems reasonable to expect that if such oxygen storage material were incorporated into the catalyst layer of a PEM fuel cell cathode, local oxygen concentration would be increased, which could in turn enhance the fuel cell performance. A Japanese patent reported that adding either vanadium oxide or zirconium oxide/cerium oxide into PEM fuel cell electrodes largely increased air utilization at a cell voltage of 0.6 V [9].

Based on a similar thought, we prepared two oxygen storage materials, $Ce_{0.8}Zr_{0.2}O_2$ and V_2O_5 , and incorporated each of them into PEM fuel cell cathodes. We did see some performance improvement for the fuel cell incorporating $Ce_{0.8}Zr_{0.2}O_2$, but the one containing V_2O_5 largely reduced the fuel cell performance. This short communication reports this study.

2. Experimental

2.1. Preparation of $Ce_{0.8}Zr_{0.2}O_2$ and V_2O_5

$Ce_{0.8}Zr_{0.2}O_2$ was prepared using $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot xH_2O$ [2]. The cerium (0.1 mol) and zirconyl

^{*} Corresponding author. Tel.: +1-973-450-4400x5560;

fax: +1-973-450-9850.

E-mail address: zqi@hpower.com (Z. Qi).

(0.025 mol) salts were dissolved in 800 ml water to form a clean solution, followed by the dropwise addition of NaOH solution (14.5 g in 100 ml water) to produce slightly yellowish slurry. The slurry was aged overnight and then collected by filtration with a thorough washing using water. The product was dried at 150 °C for 30 min, and was washed again before being calcined in air at 500 °C for 3 h. The final product had a chemical composition of $Ce_{0.8}Zr_{0.2}O_2$ based on [2].

V_2O_5 was prepared similarly by reacting $VOSO_4 \cdot xH_2O$ (0.1 mol) with NaOH (0.2 mol) in 800 ml of deionized water.

2.2. Preparation of electrodes and MEAs

Catalyst mixtures were prepared by directly mixing E-TEK 20% Pt/Vulcan XC-72, Nafion solution (5%, DuPont), and either $Ce_{0.8}Zr_{0.2}O_2$ or V_2O_5 . The Nafion content within the mixture was controlled at 23%. The mixture was stirred thoroughly before it was applied onto a carbon paper-type gas diffusion medium that contained a very homogeneous carbon/PTFE layer. The electrodes were dried in an oven at 135 °C for 30 min, and then were hot-bonded onto a Nafion 112 membrane at 130 °C for 3 min to form a membrane-electrode assembly (MEA).

2.3. Test of MEAs

Single cell tests were performed using a homemade 10-cm² active area test fixture. The test fixture was composed of a pair of metal plates with serpentine flow-fields. The

plates were coated with metal nitride for corrosion protection. Rod-like heaters were inserted into the plates to control the cell temperature. Air and pure hydrogen were used as the reactants. They were humidified by passing them through stainless steel water bottles prior to entering the cell. The cell temperature, hydrogen humidification temperature, and air humidification temperature are denoted hereinafter as $T_{cell}/T_{hydrogen}/T_{air}$. The stoichiometries of air and hydrogen were controlled to about 10× at a current density of 2.0 A/cm² using flow meters. The load was varied using a rheostat when voltage (V)–current density (*I*) curves were collected.

2.4. MEA activation by using elevated temperature (*T*) and pressure (*P*)

This elevated *T/P* activation was carried out at a cell temperature of 75 °C, hydrogen humidification temperature of 95 °C, air humidification temperature of 90 °C, hydrogen pressure of 20 psig, and air pressure of 30 psig. Such an activation condition is denoted hereinafter as 75/95/90 °C, 20/30 psig [10,11]. During the activation, the fuel cell performance was recorded every 30 min. When no further increase in performance was observed, the activation procedure was considered to be complete.

3. Results and discussion

Fig. 1 shows the performance before activation of MEAs whose cathodes contained 0, 8.3, 14.9, 22.0% $Ce_{0.8}Zr_{0.2}O_2$,

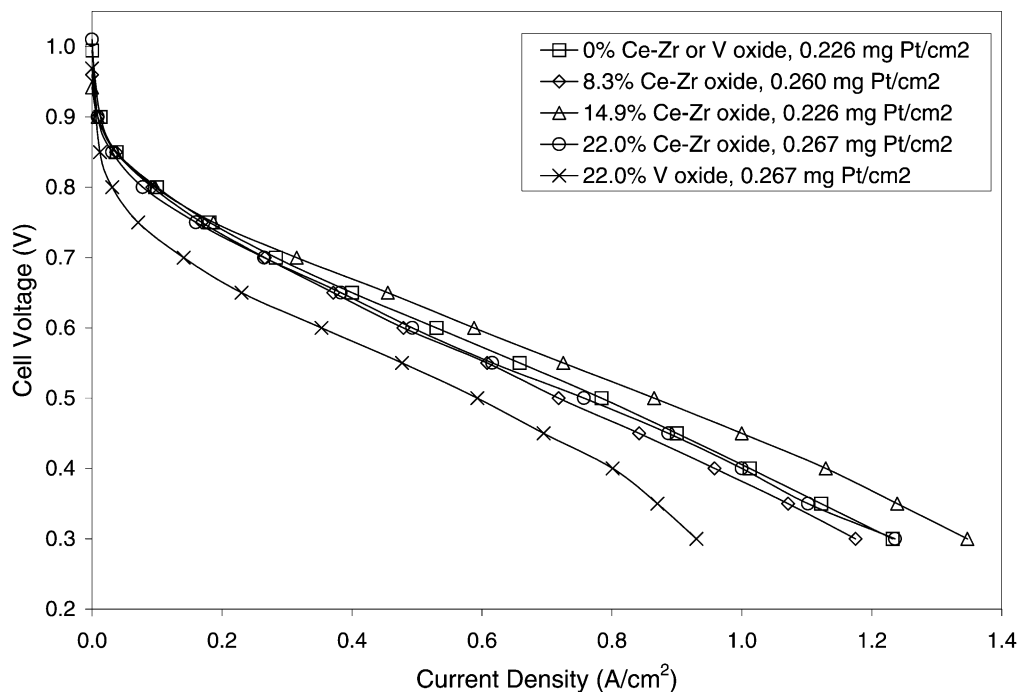


Fig. 1. Performance before activation of MEAs whose cathodes contained 0, 8.3, 14.9, 22.0% $Ce_{0.8}Zr_{0.2}O_2$, and 22.0% V_2O_5 , respectively (35/45/45 °C; E-TEK 20% Pt/C; Nafion 112 membrane).

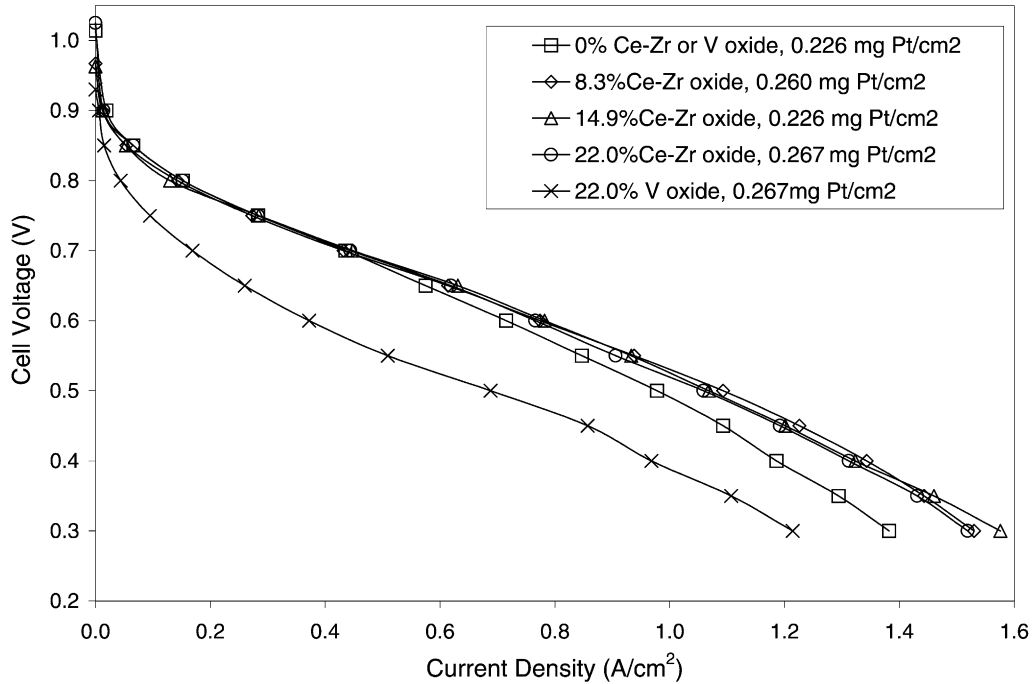


Fig. 2. Performance after activation of MEAs whose cathodes contained 0, 8.3, 14.9, 22.0% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, and 22.0% V_2O_5 , respectively (35/45/45 °C; E-TEK 20% Pt/C; Nafion 112 membrane).

and 22.0% V_2O_5 , respectively. All performance was recorded after completion of a traditional break-in procedure. In other words, the MEAs were tested at 35/45/45 °C continuously until their performance did not show further increase. The MEA containing no oxygen storage material was used as a comparison standard, a control. It can be seen that the incorporation of 8.3 and 22.0% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ slightly decreased the performance, but the incorporation of 14.9% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ obviously increased the performance. However, adding 22.0% V_2O_5 largely declined the performance.

Based on our experience, an MEA does not reach the maximum performance after a traditional break-in, and this performance does not reflect the true strength of the MEA. The performance can be largely enhanced by an activation procedure [10,11], and the performance after activation more accurately reflects the strength of the MEA. Sometimes, one MEA performs better than another one before activation, but the latter possesses a higher performance than the former after activation. The enhancement by activation is related to the composition and structure of each MEA.

In order to obtain the true performance strength of the MEAs shown in Fig. 1, these MEAs were activated at 75/95/90 °C, 20/30 psig. During the activation process, the performance was recorded every 30 min until no further increase was observed. At this point, the activation was considered to be complete. Then the temperatures were returned to 35/45/45 °C and the pressurization was released. Fig. 2 shows the performance of these MEAs after activation.

First, after activation, the performance of all MEAs increased largely. This was as expected. Second, the control MEA had the same performance as those containing

$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ at cell voltages higher than 0.70 V. But at lower cell voltages (e.g. higher current density), the three MEAs containing 8.3, 14.9, and 22.0% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, respectively, showed better performance. Third, all three MEAs containing $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ had similar performance among themselves. Finally, the performance of the MEA containing 22.0% V_2O_5 was much lower than that of the control MEA, which was contradictory to findings in a previous report [9]. Table 1 lists the current densities at a cell voltage of 0.50 V for these MEAs after activation.

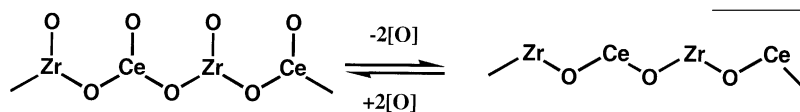
Since the performance enhancement in the presence of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ was minor, the experiments were repeated to make sure that the difference was not simply due to experimental errors.

There are various mechanisms to account for the oxygen storage capacity of CeO_2 -based materials [3,4]. One mechanism states that the distortion of the oxygen sublattice within these materials generates some mobile oxygen, and the insertion of Zr^{4+} into CeO_2 lattice strongly modifies the structure of the latter, which then enhances the oxygen mobility [3]. Another mechanism believes that the change

Table 1
Current density at 0.50 V

MEA	I (A/cm ²)
Control	0.978
8.3% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	1.093
14.9% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	1.068
22.0% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	1.059
22.0% V_2O_5	0.688

in the redox states between Ce_2O_3 and CeO_2 is responsible for the oxygen storage: when Ce_2O_3 changes to CeO_2 , oxygen is incorporated into the material; whereas, when CeO_2 changes to Ce_2O_3 , oxygen is released [4]. No matter what the mechanism is, it has been widely accepted that this class of material has the ability to store oxygen when the external oxygen concentration is high, and to release oxygen when the external oxygen concentration is low, as shown below schematically.



When our cathodes were prepared, all the electrode components were thoroughly mixed in order to achieve close contact among Pt/C, Nafion, and $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (or V_2O_5). Since $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ has the ability to store oxygen, it may provide some additional oxygen to Pt/C, especially when oxygen concentration is low in the high current density region. Therefore, the fuel cell performance increases compared to the control. However, the enhancement in performance is minor, and the performance itself is much lower than that when pure oxygen is used.

We do not know how much extra oxygen $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ can store, and how fast the stored oxygen will be released to feed the fuel cell reaction. We are not sure why V_2O_5 actually reduced the fuel cell performance. Some obvious reasons could be the dilution of Pt sites per unit volume and the increase of catalyst layer resistance caused by V_2O_5 . However, since the performance of the MEA containing V_2O_5 was lower than that of the control over the entire current density region, the major reason seemed to be that somehow V_2O_5 reduced the catalytic activity of Pt/C. More studies are needed in this area in order to better understand the effects of oxygen storage materials on the performance of PEM fuel cells.

Although $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ can store some extra oxygen, the presence of a “nitrogen blanket” remains a substantial

performance barrier; and oxygen-like performance remains far off.

4. Conclusions

Oxygen storage materials $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and V_2O_5 were prepared and incorporated into PEM fuel cell cathodes. $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ slightly enhanced the fuel cell performance

at cell voltages lower than 0.70 V. The amount of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ within the catalyst layers did not affect the performance enhancement when it was ranged from 8.3 to 22.0%. When 22.0% V_2O_5 was incorporated into a cathode, the fuel cell showed much lower performance than the control. The behavior of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and V_2O_5 within a PEM fuel cell is not fully understood.

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