RuO$_2$-BASED DENSE ELECTRODES FOR ESB ELECTROLYTE IT-SOFCs

Vincenzo Esposito$^{1,2}$, Enrico Traversa$^1$ and Eric D. Wachsman$^2$

$^1$Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata" Via della Ricerca Scientifica, 00133, Roma, Italy
$^2$Department of Materials Science and Engineering, University of Florida Gainesville, FL 32611, USA

ABSTRACT

In this work, we evaluated the performance of dense electrodes based on Ru oxides for Er$_2$O$_3$ stabilized Bi$_2$O$_3$ (ESB) electrolyte. To fabricate symmetric cells, RuO$_2$ thick films were deposited by screen printing on the parallel surface of dense ESB electrolyte pellets. A very dense layer of Er/Bi ruthenate (EBR) was formed at the interface by \textit{in situ} solid state reaction between the dense pellet (ESB) and the deposited RuO$_2$. The reaction led to the formation at the electrode/electrolyte interface of a layer with pyrochlore structure. The electrochemical performance of the EBR/ESB/EBR symmetric cell was investigated using electrochemical impedance spectroscopy (EIS) measurements in air. The dense morphology of the electrodes allowed quantification of the triple phase boundary (TPB) length and its effect on the area specific resistance (ASR).

INTRODUCTION

The performance of a solid oxide fuel cell (SOFC) is closely correlated with the properties of its components. In the electrodes, microstructural and electrochemical properties of the materials must be controlled to limit the formation of resistive phase(s) that increase electrode polarization (1, 2). Erbia stabilized bismuth oxide (ESB) has been recently proposed as the cathode side component in a new type of fast, purely ionic bi-layered electrolyte used for intermediate temperature solid oxide fuel cells (IT-SOFCs) (3, 4). In IT operative conditions, the polarization drops are large and for cells using ESB as an electrolyte new cathode materials are needed.

Ruthenium has been proposed as electrode material for low temperature fuel cells because of its catalytic activity toward oxygen in redox reactions. In addition, ruthenium based pyrochlores have been investigated for IT-SOFCs because of the low thermal stability of ruthenium. Pyrochlores can be used because of their high metallic or semiconducting electrical conductivity (5, 6) that allows application of these oxides in catalysis (7).

Bi$_2$Ru$_2$O$_{7.5}$ pyrochlore possesses electrical and catalytic properties similar to those of RuO$_2$ (6, 8-11). In this work, bismuth and erbium ruthenates (called EBR) were obtained as very dense layers by a solid state reaction of RuO$_2$ and ESB onto the external surface of dense ESB pellets. \textit{In situ} reaction allowed obtainment of continuous electrodes on the
electrolyte surfaces. Moreover, this cell configuration avoided spreading resistance effects (12) and allowed obtaining a measurable triple phase boundary (TPB) length.

Electrochemical impedance spectroscopy (EIS) measurements were used to evaluate the presence of resistive additional phase/s at the electrode/electrolyte interface as well as the influence of the TPB length on the polarization and the typical frequencies of the oxygen reduction process in EBR/ESB cells.

EXPERIMENTAL

Erbia stabilized bismuth oxide (ESB) with \((\text{Er}_2\text{O}_3)_{0.2}(\text{Bi}_2\text{O}_3)_{0.8}\) composition was prepared by solid state reaction. \(\text{Er}_2\text{O}_3\) and \(\text{Bi}_2\text{O}_3\) (Alfa Aesar), in stoichiometric ratio, were mixed in a ball mill for 24 hours. The solid state reaction was carried out at 800°C for 10 hours in air. The final powder was milled again for 48 hours and sieved, keeping the particles smaller than 1 μm. X-ray diffraction (XRD, CuKα x-rays, Philips XRD 3720) in Bragg-Brentano configuration was used for phase identification. ESB pellets were pressed isostatically at 200 MPa and sintered for 10 hours at 850°C, slightly above the \(\text{Bi}_2\text{O}_3\) melting temperature, leading to grain growth and consequent grain boundary surface decrease. ESB pellet surfaces were carefully polished to obtain a flat and smooth surface before the electrode deposition. Electrodes were fabricated starting from a commercial ruthenium oxide powder (Aldrich). \(\text{RuO}_2\) slurry was prepared using an organic binder in ethanol and ball milling overnight. Electrodes were painted and sintered at 800°C for 3 hours. Fabricated symmetric EBR/ESB/EBR samples were modified to increase the TPB length in measurable way: a 1 mm diameter diamond coated drill bit was used to make holes in the dense electrode layers. Hole shape and geometric parameters were observed by optical microscope (Nikon Epiphot).

Electrochemical impedance spectroscopy (EIS) measurements were performed using a Frequency Response Analyzer (FRA Solartron 1260) and dielectric interface (1296 Solartron). Impedance measurements were taken both on different shaped EBR/ESB/EBR cells and on a sample before and after electrode modification.

The EBR/ESB/EBR samples were placed into a quartz chamber and positioned inside a tubular furnace. Gold wires and platinum mechanical contacts were used as current collectors. Measurements were performed in a synthetic air flux at temperatures from 250°C to 700°C in the frequency range 10 mHz-1 MHz. The amplitude of the applied voltage signal was 500 mV. EIS data were analyzed using Zview® software.

In addition to the investigation of the electrical properties of the cell, reactivity tests between ESB and \(\text{RuO}_2\) were performed to understand the chemistry of the solid state reaction. ESB-\(\text{RuO}_2\) (molar ratio 1:3) composite powders and pellets uniaxially pressed and sintered at 850°C for 12 h were prepared. Simultaneous thermogravimetric and differential thermal analysis (TG/DTA, Netzsch STA 409) was carried out in air in the temperature range between 50°C and 1050°C to evaluate the ESB-\(\text{RuO}_2\) reactivity. Crystalline phases were identified by XRD analysis. The morphology and elemental composition of the samples were analyzed by field emission scanning electron microscopy (FE-SEM, JEOL 6133) and energy dispersive spectroscopy (EDS, INCA).
RESULTS

Solid state reaction between RuO$_2$ and Bi$_2$O$_3$, to obtain Bi$_2$Ru$_2$O$_{7.5}$ pyrochlore structure, is a low temperature process in air. Ruthenium oxide and ESB react at temperatures around 150°C and the structure obtained is stable in air up to 1000°C. Moreover, TG/DTA of ESB-RuO$_2$ powder mixture showed a weight loss up to 400°C due to volatilization of the RuO$_2$ excess, and a final decomposition of the product starting by 1100°C (results not shown).

Figure 1 shows the diffraction pattern of a milled ESB/RuO$_2$ pellet obtained from the powder mixture (ESB:RuO$_2$ = 1:3 molar), previously pressed and fired at 850°C for 12 hours. Solid state reaction at 850°C led to the crystallization of a pyrochlore structure. No ESB or RuO$_2$ phases were detected because of the complete reaction of the reactants and the volatilization of excess RuO$_2$. Figure 1 also shows the referenced patterns of Bi$_2$Ru$_2$O$_{7.5}$ and Er$_2$Ru$_2$O$_7$. The comparison between Bi$_2$Ru$_2$O$_{7.5}$ reference and the sample diffraction pattern showed a slight deviation of the lattice parameters. This can be ascribed to the dissolution of erbium in the Bi$_2$Ru$_2$O$_{7.5}$ phase. Such a material has metallic conductivity.

Figure 2 shows the morphology of the ruthenate electrodes obtained by the solid state reaction of RuO$_2$ slurry deposited on dense ESB pellet and fired at 800°C for 3 hours. Typical sharp pyrochlore crystals can be observed in the SEM image; Ruthenates grew on the ESB surface continuously without porosity or cracking. Elemental analysis showed the presence of Ru, Er and Bi in the ruthenate layer.

Figure 1. XRD pattern of the ESB / RuO$_2$ (1:3 molar) sample fired at 850°C for 12 hours. The figure shows the experimental (solid line) and the reference diffraction patterns of Bi$_2$Ru$_2$O$_7$ (bars corresponding to the symbol *) and Er$_2$Ru$_2$O$_7$ (bars corresponding to the symbol °).
Figure 2. FE-SEM micrograph of Bi-Er ruthenates (EBR) dense electrodes (surface) obtained by solid state reaction between ESB and RuO$_2$ at 800°C for 3 hours.

Figure 3 shows FE-SEM cross section image of a cell where dense electrodes (A) grew on the dense ESB pellet (B). The electrodes had a thickness of around 2 µm. The elemental analysis of the cell cross section did not show any relevant ruthenium diffusion through the ESB dense pellet for samples treated at 650°C in air for over 24 hours.

Figure 3. FE-SEM cross section image of Bi-Er ruthenates electrodes (A) obtained by solid state reaction on dense ESB pellet (B).

Figure 4 shows the optical microscope image of one of the holes. The diameter is about 2 mm. The total number of holes is ten (5 on each side) and the ratio between the hole area and total area of the electrodes 0.18. Thus, less of the 20% of the electrode area is covered by the holes. Having a dense morphology for the electrodes allows also to calculate the increase in the TPB length: the TPB length after hole incorporation was measured to be 1.98 times the TPB length of the dense electrode sample.
EBR/ESB/EBR symmetric cells were tested using EIS in air in the 250-700°C temperature range. At low temperatures (250°C < T < 400°C), it is possible to separate the impedances related to each cell component. Figure 5 shows a typical impedance plot of an EBR/ESB/EBR symmetric cell tested in air at 250°C. The ESB electrolyte impedance is attributable to the semicircle at high frequencies (f > 1 kHz). No interfacial impedance contributions at lower frequencies were detected (3).

EIS analysis of electrodes polarization in air, at temperatures around 600-700°C allows evaluation of the cathodic overpotential, which is related to the rate limiting step of the electrochemical processes (14).
In SOFCs, the area specific resistance (ASR) (13) is defined as:

\[ \text{ASR} = R_{\text{chem}} A_{\text{electrode}} \]

where \( A_{\text{electrode}} \) is the electrode/electrolyte area of the cell and \( R_{\text{chem}} \) is the resistance due to the electrodes polarization (low frequencies contribution) (14). Low ASR values imply better SOFC performance. The ASR was divided by 2 due to the cell symmetry (see definitions of ASR in 13,14).

EIS measurements of an EBR/ESB/EBR cell were performed in the 250-700°C temperature range, and Figure 6 shows typical impedance plots measured at 600°C before (\( L_0 \)) and after (\( L' \)) modification of the electrode by hole incorporation. The plots show a significant decrease of the semiarc at low frequencies after hole incorporation, resulting in a significant ASR decrement: at 600°C, the measured ASR decreased from 5.4 Ω cm\(^2\) to 0.63 Ω cm\(^2\) after electrode modification. The reduction of the electrode area was 20% while the decrease in ASR is much larger. This can be explained in terms of a variation of the polarization resistance due to the increase in the TPB length. This explanation is univocal because of the peculiar morphology of the tested electrodes, which were completely dense.

Another important feature evidenced in Figure 6 is the dramatic change in the relaxation frequency of the low-frequency semiarc, which shifted from 40 mHz to 1 Hz after hole incorporation. This relaxation frequency indicates the time necessary to discharge the electrodes. This proves that the increase in TPB is effective in reducing electrode polarization, and this effect can be quantified in the present system given the peculiar morphology of the studied electrodes. Considering that the EBR electrodes are dense and purely electronic conductors, processes like gas diffusion and oxygen sorption-desorption at the gas-cathode interface can be discarded. The obtained results demonstrate that the rate limiting step of the electrode reactions is due to phenomena occurring at the TPB (3 and ref. therein), i.e., oxygen sorption-desorption at the TPB and charge transfer at the electrode-electrolyte interface.

Figure 6. Complex impedance plane plots for EBR/ESB/EBR symmetric cells measured in air at 600°C with TPB=\( L_0 \) (circles) and TPB=\( L' \) (squares).
CONCLUSIONS

Pyrochlore (Er, Bi) ruthenate (EBR) dense electrodes were synthesized by an in situ solid state reaction between a dense ESB electrolyte substrate and ruthenium oxide powders, to obtain EBR/ESB symmetric cells. EIS measurements were used to evaluate the electrochemical properties of EBR electrodes. At low temperatures ($250^\circ C < T < 400^\circ C$), no interfacial impedance components were observed for the electrode-electrolyte interface. The dense morphology of the electrodes allowed increasing the TPB in a quantitative manner upon incorporation of holes in the electrode surface. TPB extension led to a significant reduction of ASR values. Specifically, an 80% reduction in $R_{\text{chem}}$ was observed at $600^\circ C$ for incorporation of holes through the EBR layer covering an area of only 20% of the electrode area, indicating the paramount importance of TPB length in electrode polarization processes.

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