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Wide bandgap oxides for single-layered nanocomposite fuel cell

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Abstract

A composite of wide bandgap lithium-nickel-zinc-oxide (LNZ) and gadolinium-doped-cerium-oxide (GDC) was systematically analyzed for a low-temperature nanocomposite fuel cell in a so-called single-component configuration in which the electrodes and electrolyte form a homogenous mixture. We found that the operational principle of a single-layer fuel cell can be explained by electronic blocking by the oxide mixture with almost insulator-like properties in the operating voltage regime of the fuel cell, which will prevent short-circuiting, and by its catalytic properties that drive the fuel cell HOR and ORR reactions. The resistance to charge transport and leakage currents are dominant performance limiting factors of the single-component fuel cell. A test cell with Au as current collector reached a power density of 357 mWcm^{-2} at 550°C . Changing the current collector to a $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL) coated Ni foam produced 801 mWcm^{-2} , explained by better catalytic properties. However, utilizing NCAL coated Ni foam may actually turn the 1-layer fuel cell device into a traditional 3-layer (anode-electrolyte-cathode) structure. This work will help in improving the understanding of the underlying mechanisms of a single-layer fuel cell device important to further develop this potential energy technology.

Key words: bandgap; ceramic; fuel cell; ionic conductivity; nanocomposite; single-component

1. Introduction

Nanocomposite ceramic fuel cells have recently gained much attention in the fuel cell research community [1–15]. The latest development include a so-called single-component or single-layer fuel cell in which the three distinct layers of a traditional fuel cell (cathode-electrolyte-anode) are replaced with a single homogenous composite layer consisting of electrolyte and electrode materials, basically a mixture of semiconducting and ionic materials [2,7,9,10,15]. All fuel cell processes occur in this 1-layer structure unlike in a conventional 3-layer structure, where each layer has a distinctive function for electrode reactions, electron separation, and ionic transport, etc. Surprisingly, power densities up to 1 Wcm^{-2} (with H_2 at 550°C) have been reported using the single layer cell configuration [12–14], which is beyond the power density of a standard 3-layer solid oxide fuel cell based on yttrium stabilized zirconia (YSZ) or samarium/gadolinium doped ceria (SDC/GDC) electrolyte with perovskite structured electrodes such as lanthanum strontium manganite (LSM) and lanthanum strontium cobalt ferrite (LSCF) [16–18]. However, the spread of reported performance is large in the range $200\text{--}1,000 \text{ mWcm}^{-2}$ even under similar operational conditions. Some of these variations could be attributed to different material systems and cell manufacturing methods, but even identical cells have shown large differences.

Such high performance values for a semiconductor-ionic material composition compared to the state-of-the-art of low-temperature (LT) SOFC (ca $1,000 \text{ mWcm}^{-2}$ at 550°C) [19] give rise to several fundamental questions about the mechanisms in the cell. In particular, how electric short-circuiting is prevented (in a conventional 3-layer fuel cell the electrolyte layer handles this)? How can the fuel cell perform so well without porous electrodes typical to traditional solid oxide fuel cells? The present stand of understanding is that p-n, Schottky, or bulk heterojunctions created by the oxides in the material mixture attribute to protecting against short circuiting [9,10,12]. The porosity issue or the surface area of the catalytic material, which is crucial to efficient reaction kinetics in the cells have,

however, not been addressed so far in the single-layer fuel cell literature. Furthermore, it is observed that although these cells have been regarded as a 1-layer or single-component fuel cell, Ni foam coated with $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL) are often used as current collectors. Both Ni and NCAL have catalytic properties to support electrode reactions [14,20], and therefore these could potentially act as an electrode and the composite layer of the electrolyte and electrode material could act as an electrolyte layer, and consequently the device could work like a typical 3-layer structured device, or a LT-SOFC. Such a device with a single layer of NCAL-NSDC has been reported to reach 1.07 W/cm^2 in a single cell configuration[14]. Furthermore, NCAL is a typical electrode material in lithium ion batteries [21–23], and it is conceivable that reactions other than oxygen-reduction reaction (ORR) and hydrogen-oxidation reaction (HOR) could also occur in the cell, which could affect the long-term stability of the device. However, single-component fuel cells with non-catalytic current collectors (Ag) have also been employed [7,8], which confirm the operational principle of a 1-layer structure, but with much lower performance.

The aim of this study was to verify the operational principle of a single-layer fuel cell, and in particular to understand how the choice of the current collector material could influence its performance e.g. through catalytic mechanisms on the interface. We fabricate a real single-layer nanocomposite fuel cell avoiding any catalytic interventions from the current collector material, which we then compared to a device configuration, in which catalytic current collector material was employed. The single-layer fuel cells were fabricated from wide bandgap lithium-nickel-zinc-oxide (LNZ) and gadolinium-doped-cerium-oxide (GDC) nanoparticles (40-70 nm) using Au current collectors. LNZ functions as an electrode material and GDC as an ionic conductor, respectively. Different layer thicknesses and gas atmospheres were used to investigate the operational mechanisms of the cell, e.g. which kind of ion dominates ionic conduction in the cell. The pressing method was used to fabricate the fuel cell samples (diameter=13 mm). The cells were characterized using different electrochemical (current-voltage polarization (IV), electrochemical impedance spectroscopy (EIS)),

spectroscopic (UV-Vis reflectance measurement), and microscopic (scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), energy dispersive spectroscopy (EDX)) methods. A schematic structure of the single layer ceramic nanocomposite fuel cell is shown in the Fig. 1. In fuel cell operation mode, hydrogen and oxygen gases are supplied to the respective sides of the cell. The oxidation of hydrogen gas into hydrogen ions takes place on one side and reduction of the oxygen gas into oxide ions happens on the opposite side, which results in multi-ionic conduction in the cell.

Figure 1. Schematic structure of a single layer ceramic fuel cell.

2. Experimental section

2.1 Materials and fabrication

All the chemicals used in the experiment were purchased from Sigma Aldrich. Commercial gadolinium doped ceria (GDC) nanopowder was used as ion conducting material to minimize the uncertainties in the compositions during the sample preparation. The catalytic material was synthesized through the solid route. Li_2CO_3 , $\text{NiCO}_3 \cdot 2\text{Ni(OH)}_2 \cdot x\text{H}_2\text{O}$ and $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed, ground, and then sintered in an oven at 800°C for 3 hours. The molar composition of the metal elements was $\text{Li} : \text{Ni} : \text{Zn} = 3 : 9 : 8$. This composition of the catalytic material was chosen in this study because single component fuel cell has been reported in the literature using the same composition of electrode material and produced 600 mW/cm^2 at 550°C [3]. This material is abbreviated as LNZ.

The GDC and LNZ powders were mixed in a ball milling machine in a ratio of 60:40 wt%, respectively. After mixing, the powder was sintered at 700°C for 4 h followed by a vigorous grinding in a mortar for 20 min. The resulting composite powder was used to fabricate the single component fuel cells by pressing method by pressing it with a pressure of 250 MPa for 2 minutes in a 13 mm diameter die. The single layer pellets were sintered at 700°C for an hour. Finally, gold paste was applied on both sides of the most of the fuel cell pellets to improve the electrical contact for fuel cell measurements. For another set of the cells, NCAL coated Ni foam was applied on both sides of the cells for the current collection.

2.2 Characterization techniques

The electrochemical measurements were performed using a Probostat from NorECs Ltd. Prior to the measurements, the cells were sealed in the Probostat using a ceramic adhesive, Ceramabond 552 from Aremco, to prevent the gas mixing between the inner and outer chambers of the Probostat. The electrical connections in the Probostat were done using gold wires. A K type thermocouple was placed near the cell in the outer chamber of the Probostat. It is important to place the K type thermocouples on the cathode side of the cell as they may degrade in the presence of hydrogen gas at high temperature

and give wrong temperature reading. After the necessary arrangements were ready, the Probostat was placed in a furnace and the electrochemical measurements were performed using an impedance measurement unit, Zahner Elektrik's IM6. The electrochemical impedance spectroscopy (EIS) measurements were conducted at open-circuit-voltage (OCV) of the cells using an AC amplitude of 20 mV and a sweeping frequency range from 100 mHz to 100 kHz. The current density-voltage (IV) and current density - power density measurements (IP) of the cells were performed at 550°C in the presence of H₂ at anode and air at cathode. The slew rate of the measurements was 20 mV per sec. An XRD unit (PANalytical X'Pert PRO MPD, Rigaku Smarta) was used to measure the crystal structure of the materials. The measurements were conducted on the powders at room temperature using Cu K α_1 radiation (45 kV and 40 mA; $\lambda = 1.5406 \text{ \AA}$). An analytical high-resolution transmission electron microscope (HR-TEM, Jeol JEM-2800) was used to analyze the particle size and the crystal orientations. A field emission scanning electron microscope (FE-SEM, Zeiss Sigma VP) was utilized to examine the morphology of the cells. The Brunauer-Emmett-Teller (BET) analysis (Micromeritics TriStar 3020) was performed to measure the specific surface area of the composite cell.

3. Results and discussion

The band gaps of Li₂O, NiO, ZnO are 16.7 eV [24], 3.6 - 4 eV [25] and 3.3 eV [26], respectively. The bandgap 3.6 eV of the LNZ nanopowder material (particle size 20-70 nm) was determined optically through reflectance measurements as shown in the Fig. 2a. These oxides are thus wide bandgap materials in which the electron conductivity is quite low at room temperature. Operating at a higher temperature would decrease the band gap according to the Varshni equation [27], which would slightly improve the electronic conduction. The electronic conduction depends on both the mobility of the electrons and the charge carrier concentration. Generally, at temperatures higher than 200 K, the mobility of the electrons is limited by the lattice scattering and decrease as a function of temperature $\mu \propto T^{-n}$, where $n < 2$ for a single lattice scattering process [28]. On the other hand, at high temperatures the thermally generated intrinsic carriers would dominate and

improve the electronic conduction. Therefore, the composite of LNZ and GDC can support both the ionic and the electronic conduction to certain extent. The XRD spectrum in Fig. 2b showed the characteristics peaks of the GDC and LNZ, confirming successful synthesis of the composite material. The peaks were identified by the International Centre for Diffraction Data (ICDD) database file no. 04-015-2396 for GDC and files no. 04-006-8078 and No. 04-013-7260 for LNZ.

In principle, due to the presence of different bandgap materials bulk junctions exist in a fuel cell in which the anodic reactions occur on p-type material (NiO) and the cathodic reactions on n-type material (ZnO) [10]. As a result, hydrogen ions and oxygen ions are generated at the surface of the fuel side and the air side, respectively. To balance the charge neutrality, electrons are activated and accumulated on the air side. Short circuiting may be prevented due to the depletion of the charge carriers in the heterojunction formed by the semiconducting oxide components in the mixture, which forces the electrons to move through an external circuit. The cell reactions ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ at the fuel side and $\frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ at the air side) would shift the Fermi levels accordingly. The Fermi level would split only near the junction and the recombination would occur at the interfacial states due to the limited diffusion length of the minority carriers. If all the reactions occur far enough from the junction, the situation is similar to a diode that is under a reverse bias and the electrical circuit is similar to Fig. 2c, where R_e , R_l and R_i represents the resistances for electrical leakage, load, and ionic transport, respectively. In this case, the leakage current would increase to the saturation value. However, its magnitude depends on the materials used. If the saturation current is very high, the electrical resistance will also restrict the current at high leakage currents. Nevertheless, the cell can function only if the ionic conductivity is high enough for the ions to pass from one reaction site to another. If the ionic conductivity of the cell material were significantly higher than that of an electrolyte of a traditional fuel cell, the performance of a single layer fuel cell could be significantly improved over a traditional fuel cell (e.g. solid-oxide fuel cell). Figure 2d shows a typical current-voltage curve of the diode in Fig. 2c representing the heterojunction in a single-component fuel cell. Based on the typical operational voltage regime of the single-

component fuel cell (<1.2 V), the cell most likely operates in the linear region of the diode curve, since the junction is formed by the wide bandgap oxides (bandgap 3.6 eV) where resistance of the cell and the leakage currents dominate the cell performance.

Figure 2. a) UV-Vis reflectance measurements, b) XRD of the LNZ-GDC composite powder, c) device equivalent circuit model for the nanocomposite fuel cell, d) current-voltage characteristics of the diode shown in Fig. 2c.

The structure of the nanopowder of GDC and LNZ composite was analyzed by HR-TEM in Fig. 3a. The particles size of the sample was on average 50 nm, with a spread of 20 – 70 nm. The atoms and their crystal orientations are well visible in the image. Fast Fourier transform (FFT) of the HR-TEM image is shown in Fig. 3b. The spacing d between lattice planes was obtained by masking and then applying inverse FFT. Different d -spacing values (1.52 Å, 1.98 Å, 2.82 Å, 3.26 Å) were obtained as

shown in Fig. 3b. Reliability of these values depends on the accuracy of calibration done during the measurements. The d-spacing values obtained from the strongest signals of the compounds in XRD spectra shown in Fig. 2b are 3.13 Å (111) plane of GDC, 2.08 Å (200) and 1.47 Å (220) planes of NiO and 2.47 Å (101) plane of ZnO, which are reasonably close to the values shown in Fig. 3b. EDX measurements (Fig. 3c) confirmed the presence of Gd, Ce, O, Ni, and Zn. The signals from Cu and C originate from the measurement grid. Li was not detected due to its small size. The morphology of the GDC+LNZ pellet was further analyzed with SEM in Fig. 3d, showing that the nanoparticles formed clusters of 100-250 nm. Brunauer-Emmett-Teller (BET) analysis revealed a low surface area (0.78 m²/g) of the pellet, i.e. the nanoparticles were densely packed. Such a high densification of the single composite layer is favourable for efficient ionic transport in the cell, but the ORR and HOR reaction sites would be limited due to the low surface area. A low surface area would unlikely enable a high current density required to generate a high power density reported in the literature [7,12–14]. This strengthens the view that a NCAL coated NiO as a current collector, which is porous, could actually boost the cell performance and result in a higher current density by practically improving the reaction site density. To improve the current collection, we employed on both sides of the cell a porous non-catalytic layer of Au particles (particle sizes 100-300 nm, layer thickness 5-10 μm) as shown in Fig. 3e.

Figure 3. (a&b) HR-TEM image of the GDC+NLZ composite powder, and image after applying FFT filter, (c) EDX of the GDC+LNZ sample, (d&e) SEM images of the dense single layer pellet and the porous Au current collector, respectively.

The electrochemical performance of the single layer cells was measured at 550°C under different gas atmospheres (H_2/air , H_2/N_2 , N_2/air) to analyze performance limiting factors in these devices and to determine which ions dominate the conduction mechanism in the cells. Although the open-circuit voltage of these fuel cells do not exceed 1.2 V, the current-voltage (IV) curves were measured in a potentiostatic mode over a large voltage range (-4V to 4V) to compare the results with previously published data [9,10,12]. Furthermore, cells with different thicknesses (1, 2, and 3 mm) were used to analyze the pattern of increase in the cell resistance with increase in the cell thickness, which is expected to be proportional if the performance of the cell is limited by the Ohmic resistance only. The set of cells measured under H_2/air atmosphere produced output power densities of 190 mW/cm^2 (1 mm), 132 mW/cm^2 (2 mm), and 6 mW/cm^2 (3 mm) with open circuit voltages of 0.74 V, 0.70 V and 0.66 V, respectively. The total resistances obtained from the IV curves showed a gradual

increase ($1.07 \Omega\cdot\text{cm}^2$, $1.37 \Omega\cdot\text{cm}^2$ and $3.51 \Omega\cdot\text{cm}^2$ for cell thickness of 1 mm, 2 mm and 3 mm, respectively) as shown in Fig. 4a. The voltage range $V = 0 - \text{OCV}$ corresponds to the operational range of the fuel cell, whereas outside this region the fuel cell is more or less a passive resistor. The cells were further characterized with electrochemical impedance spectroscopy (EIS) to obtain the total cell resistance of the cells using an equivalent model reported in our previous studies [29–31]. The values obtained through EIS were quite close to the values obtained through the IV curves. For instance, for cells measured under H_2/air condition, the resistance values obtained through EIS (shown in Fig. 4d) were $1.03 \Omega\cdot\text{cm}^2$ (-3.7%), $1.49 \Omega\cdot\text{cm}^2$ (+8.8%) and $3.72 \Omega\cdot\text{cm}^2$ (+6.0%) for 1 mm, 2mm and 3 mm thick cells, respectively. The %-values in parenthesis are the deviations from the resistance values measured from the I-V curves. Increasing the thickness of the cell will increase the Ohmic losses, which limits the performance.

The fluorite structure of CeO_2 doped with Gd primarily supports the oxygen ion conduction through the oxygen vacancies created by the substitution of tetravalent Ce atom with the trivalent Gd atom [32]. Heavy doping of CeO_2 with Gd could create high concentration of oxygen vacancies for the sake of electroneutrality. However, above a certain doping level (>30%) the fluorite structure would transform into a cubic superstructure due to the reorganization of the oxygen vacancies [33]. The ionic conductivity in the cubic superstructure could be decreased due to the immobility of the vacancies in this superstructure [33,34]. Therefore, in this study 20% Gd doped CeO_2 was used at which the fluorite crystal structure remains stable and efficiently supports oxygen ion conduction through the vacancies. In addition, the conduction of hydrogen ions through a hopping mechanism at the interfaces of the doped ceria particles have been reported [35–37]. The oxygen-reduction reaction (ORR) and hydrogen-oxidation reaction (HOR) of the cell is shown in reactions (1-3) below. The oxygen ions primarily move through the vacancies in the oxide phase [38], whereas hydrogen ion conducts through a hopping mechanism on the protonated oxides in the cell [39]. The following reactions characterize the fuel cell operation:

To investigate the role of H^+ and O^{2-} in the ionic conductance, we analyzed the three cell types under different gas atmospheres. Starting with a H_2/N_2 atmosphere (Fig. 4b) the total resistances obtained from the polarization curve ($1.17 \, \Omega\cdot\text{cm}^2$, $1.96 \, \Omega\cdot\text{cm}^2$ and $4.17 \, \Omega\cdot\text{cm}^2$) and EIS ($1.19 \, \Omega\cdot\text{cm}^2$, $2.07 \, \Omega\cdot\text{cm}^2$ and $5.08 \, \Omega\cdot\text{cm}^2$) were quite similar. The values are slightly higher than those obtained in H_2/air atmospheres. In the H_2/N_2 case, only hydrogen ions could have contributed to the ionic conductivity of the cell, as oxygen gas was absent. This indicates a dominant hydrogen ion transport mode.

Figure 4. Current-voltage curves of single layer fuel cells of different thicknesses (1 mm, 2mm, 3 mm) at 550°C under different gas atmospheres (a) H₂ and air on opposite sides of the cells, (b) H₂ and N₂ on respected side of the cells, (c) N₂ and air on respected side of the cells, (d) the electrochemical impedance spectra at open circuit voltage condition.

The cell resistances in a N₂/air atmosphere dramatically increased compared to the case with H₂/N₂ as shown in Fig. 4c The cell resistances were now 3.35 $\Omega\cdot\text{cm}^2$, 32.21 $\Omega\cdot\text{cm}^2$ and 104.63 $\Omega\cdot\text{cm}^2$ (from IV curve); and 4.01 $\Omega\cdot\text{cm}^2$, 23.90 $\Omega\cdot\text{cm}^2$ and 94.81 $\Omega\cdot\text{cm}^2$ from the EIS. The increase in the cell resistance vs. increasing the cell thickness was much steeper than in the previous cases with H₂/air and H₂/N₂ atmospheres. In the N₂/air atmosphere, the ionic conduction is dominated by oxygen ions as no hydrogen was fed into the cell. The dramatic increase in the cells' resistive losses indicates, however, sluggish oxygen ion conduction. Based on these results, we conclude that the main ionic transport mechanism in the single layer fuel cell with LNZ+GDC as the base material is hydrogen ion transport.

Several cells with LNZ+GDC and Au current collectors were analyzed. The best cell yielded 357 Wcm^{-2} at 550 °C with hydrogen as shown in Fig. 5. The spread among the test cells was 100-357 Wcm^{-2} , which also illustrates the sensitivity of the performance to device structures and measurement configurations. Replacing the current collectors with Ni/NCAL yielded 801 mWcm^{-2} for the best sample shown in Fig. 5. The doubling of the performance cannot be only explained by measurement statistics, but would most likely originate from the increased catalytic activity and porosity due to NCAL/Ni. An earlier study with a similar material system and Ag current collector reported also 800 Wcm^{-2} , but they used in addition a carbonate with GDC, which most likely boosted the performance through additional ionic conductivity from carbonate ions (CO_3^{2-}) [7] – such a fuel cell system would also need CO₂ feeding to operate in a stable way. Recently, the scientific community has also raised concerns on measurement procedures and inaccuracies of

single-component fuel cells [40], which may narrow down some of the differences in results found in various studies.

Figure 5. Comparison of the performance of single component fuel cells utilizing Ni foam coated $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL) as current collector on both sides of the cell and Au as current collector on both sides of the cell measured at 550°C (H_2 and air were supplied on the respected sides of the cell).

4. Conclusions

We have shown here that the operating principle of a single component nanocomposite fuel cell can be explained through electron blocking of the resistance and catalytic activity of a wide bandgap oxide. We used a composite of lithium-nickel-zinc-oxide (electrode material) and gadolinium-doped-cerium-oxide (ionic conductor). The resistance to the transport of charge carriers and leakage currents would be the dominant performance limiting factors of the 1-layer fuel cell. Furthermore,

we found that H^+ dominates the ionic transport in the cell, whereas the contribution from the O^{2-} ions is minor.

The fuel cell was made of a homogenous mixture of LNZ-GDC and to ensure a truly 1-layer fuel cell configuration, non-catalytic Au current collectors were employed. The best device constructed reached a 357 mW/cm^2 power density. It seems that higher performance values in the range of 1 W/cm^2 found in the literature could be related to the Ni/NCAL current collectors used that exhibit catalytic effects. Actually, replacing the current collectors with Ni/NCAL yielded in our case 801 mWcm^{-2} . A dense 1-layer cell would improbably reach such high performance as a large specific surface area would be required for efficient catalysis. But such a cell may not correspond to the original 1-layer device and would resemble more the traditional 3-layer fuel cell. One possibility to improve the single layer fuel cell further could be to use a dense layer sandwiched with porous layers of the same material. Such a structure could also be more thermally stable as the thermal expansion coefficient of the layers remain the same compared to a traditional 3-layer cell.

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