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$La_2NiO_{4+\delta}$ as oxygen electrode in reversible solid oxide cells

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Abstract

The delamination of oxygen electrode during the electrolysis mode operation, which is mainly attributed to interfacial stress arising from the inability of oxygen electrode to accommodate oxygen species transported by oxide ion conducting electrolyte at the three phase boundary (TPB), has been major concern in the development of reversible solid oxide cell (RSOC) systems. The use of lanthanum nickelate, $La_2NiO_{4+\delta}$ (LNO) as a RSOC oxygen electrode, because of its ability to accommodate excess oxygen species in interstitial positions, can be helpful in reliving such interfacial stresses and thus mitigating the problem of delamination. In this work, the possibility of using LNO as an oxygen electrode in RSOCs is examined. The button cells with 10% gadolinium doped ceria (GDC10) electrolyte, Ni-GDC10 fuel electrode and LNO oxygen electrode are fabricated and their current–voltage–power (*I–V–P*) performance is analyzed in different gas conditions while operating in fuel cell mode in 500–650 °C range. The button cell shows a maximum power density of $\sim$0.19 W cm^{-2} at a current density of $\sim$0.5 A cm^{-2} at 650 °C. Electrochemical impedance spectroscopy was performed in open circuit voltage (OCV) condition to analyze the various factors affecting the fuel cell performance. The long term operation of the fuel cell at a fixed input current of 0.1 A cm^{-2} for 100 h at 600 °C indicates that the fuel cell is capable of stable performance. The microstructural analysis of the fuel cell after the long term operations indicates no structural degradation.

Keywords: Reversible solid oxide cells; Oxygen electrode; Mixed ionic–electronic conductor; Lanthanum nickelate

1. Introduction

Reversible solid oxide cells capable of working in solid oxide fuel cell (SOFC) mode for power generation from fuel and as solid oxide electrolysis cell (SOEC) mode for fuel generation form the electrolysis of steam and CO_2 have generated widespread interest for the development of environmentally friendly ways of energy storage and electricity generation [1,2], because a RSOC system could provide effective and flexible power delivery and has the potential to be used as an efficient electrical energy storage device at the power plants based on intermittent renewable energy sources [3,4], and also provides the possibility of utilization of waste heat generated by high temperature industrial processes and excess electricity produced in off-peak hours at conventional power plants and renewable sources for steam electrolysis or steam/CO_2 co-electrolysis in SOEC mode [5,6].

Although in principle the SOEC is a reverse mode of SOFC, individual modes presents somewhat different conditions at the electrodes during its operation. Therefore, the selection of suitable electrolyte and electrode materials compatible for stable operation in SOFC mode as well as in SOEC mode is important factor for designing a RSOC. The RSOCs operating in electrolysis mode suffer from the performance degradation during the long term operations. Apart from the various reasons, such as the cation segregation and phase separation in different cell components and their interfaces, chromium diffusion from the ferritic stainless steel bipolar plate towards the electrode/electrolyte interface, the oxygen electrode delamination has been reported to be the major

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one [7,8]. Though the performance degradation due to the other reasons can be in both SOEC and SOFC modes, oxygen electrode delamination has been found to be more specific to the SOEC mode [8]. The oxygen electrode delamination may happen because of the pressure built-up due to the release of oxygen into the closed pores existing in the electrode/electrolyte interface [9]. Nevertheless, the oxygen electrode delamination can also occur due to the stress arising from the accumulation of the oxygen-ions at the electrolyte/electrode interface. During the electrolysis mode of the RSOC, the oxygen-ion transported by the electrolyte is converted to molecular oxygen at the oxygen electrode. The oxygen ion conductivity of the most commonly used air electrode strontium doped lanthanum manganite (LSM) or other mixed ionic–electronic conductors (MIECs) is much lower than that of the yttria stabilized zirconia (YSZ) in SOECs. Therefore, the oxygen electrode delamination occurs not only due to the buildup of high oxygen pressure within the electrolyte and at the anode/electrolyte interface due to differences in ionic and electronic conductivity between the electrode and the electrolyte [8], but also due to the differences in oxygen-ion conductivities of the electrode and the electrolyte. The fact is that the normal MIEC oxygen electrodes lack sufficient numbers of oxygen-defect sites (oxygen vacancy/oxygen interstitials) in electrode at the electrolyte/electrode interface to easily accommodate the oxygen-ion transported by the electrolyte. The stress arising from the mismatch of the oxygen ion conductivities of electrolyte and electrode can be mitigated if the oxygen electrode has enough defect sites to accommodate oxygen-ion before being converted to the molecular oxygen.

Mixed ionic–electronic conductors based on the Ruddlesden–Popper phases have recently attracted significant attention as alternative cathodes in place of the conventional perovskites for the intermediate-temperature solid oxide fuel cells (IT-SOFCs) [10]. The Ruddlesden–Popper phases with the K_2NiF_4-type structure, such as $La_2NiO_{4+\delta}$, have high oxygen-hyperstoichiometry and show high oxygen diffusion coefficient and high oxygen ion conductivity [11–13], which are attributes of their crystal structure consisting of alternating $LaNiO_3$ perovskite and LaO rock salt layers. The oxygen excess in $La_2NiO_{4+\delta}$ is associated with the incorporation of interstitial oxygen (O''_i) into the rock salt layers with the equivalent number of holes ($h^\bullet$) in the $LaNiO_3$ perovskite layers to maintain the charge neutrality of the system [14]. The possibility of accommodating the excess oxygen species at the interstitial sites in these materials can be helpful in lowering the stress at the electrolyte/electrode interface during SOEC operations, and therefore, LNO bases materials can be good oxygen electrodes for SOECs.

In order to ensure unhindered energy supply in more efficient and economical manner, the research on solid oxide based fuel cells and electrolyzes has been more inclined towards the development of reversible systems which can be operated equally efficiently in both SOFC and SOEC modes. The LNO-based materials, which are being widely considered as alternative cathodes for SOFCs, can be stable oxygen electrodes for SOECs as well, because of their wide range of oxygen hyperstoichiometry and its potential role in lowering the stress at the electrode/electrolyte interface, as discussed above. Therefore, it is highly imperative to explore the possibility of using LNO-based materials as oxygen electrodes in RSOCs. The present work is an attempt to explore the possibility of using LNO-based materials as oxygen electrode in RSOCs by presenting the data of SOFC operation of a fuel cell with LNO oxygen electrode. With the above mentioned objective, in this work the button cells with 10% gadolinium doped ceria electrolyte, Ni-GDC10 fuel electrode and LNO oxygen electrode are fabricated and their *I–V–P* performance is analyzed during the operations in fuel cell mode in different gas conditions in 500–650 °C range.

2. Experimental

2.1. Materials syntheses and button cell fabrication

NiO-GDC10 anode support (AS) substrates was fabricated by tape casting method [15]. The mixture slurry of NiO (Kceracell; $BET=4–6\ m^2\ g^{-1}$, $d_{50}=0.3–0.6\ \mu m$) and $Ce_{0.9}Gd_{0.1}O_{1.95}$ (Kceracell; $BET=5–8\ m^2\ g^{-1}$, $d_{50}=0.3–0.5\ \mu m$) was prepared in two steps. First, NiO and GDC10 powders were dispersed with fish oil (Aldrich) as a dispersant in a binary solvent (toluene:ethyl alcohol = 1:1 wt%) system for 24 h by ball-mill. Then, butyl benzyl phthalate, polyethylene glycol and polyvinyl butyral were added as plasticizer and binder, and the mixture was ball milled for 24 h. The de-airing process was conducted to remove the air bubbles from the slurry. NiO-GDC10 anode support tapes were fabricated by tape casting process and the obtained green sheet (thickness ~300 μm) was punched in the form of 25 mm diameter circle, to be used as AS in the fabrication of button cell assembly. Finally, the cut anode tapes were partially sintered at 900 °C for 2 h.

NiO-GDC10 anode functional layer (AFL) was coated by dip coating method. The AFL coating slurry of NiO (Kceracell; $BET=8–12\ m^2\ g^{-1}$, $d_{50}=0.2–0.5\ \mu m$) and GDC10 was prepared in an ethanol based solvent [15]. Then, the AFL coated samples were heat-treated at 400 °C for 2 h to burn out the organics materials present in the coating slurry. GDC10 electrolyte was coated on the prepared AFL coated sample by dip coating method to form AS/AFL assembly. The electrolyte coating slurry of GDC10 (Kceracell; $BET=10–15\ m^2\ g^{-1}$, $d_{50}=0.3–0.6\ \mu m$) was also prepared in an ethanol based solvent [15]. The GDC10 electrolyte layer was coated onto the as-prepared AS/AFL assembly by dip-coating the electrolyte coating slurry. Finally, the AS/AFL/electrolyte assembly was sintered at 1450 °C for 5 h in air atmosphere.

The $La_2NiO_{4+\delta}$ powder was prepared using lanthanum(III) acetate hydrate (99.9%, Aldrich, USA) and nickel(II) acetate tetrahydrate (98%, Aldrich, USA) as the starting materials by a co-precipitation method similar to that previously reported [13,16]. The $La_2NiO_{4+\delta}$ paste was prepared using planetary centrifugal mixer (Thinky, AR-100) with a texanol-based vehicle (ESL, type-441) to evaluate the electrochemical characteristics as cathode for IT-SOFC. The slurry was coated onto the electrolyte side of the AS/AFL/electrolyte assembly by screen printing method to complete the assembly of button cell. Finally, the button cell assembly was fired at 1100 °C for