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Interpretation of an inductive loop in the impedance of the impregnated $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$Y_2O_3$ stabilized ZrO_2 cathodes

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ABSTRACT

The electrocatalytic performance of the impregnated $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-Y_2O_3 stabilized ZrO_2 (YSZ) cathodes has been investigated by electrochemical impedance spectroscopy (EIS) using a "three-electrode" configuration for intermediate temperature solid oxide fuel cells. The significant inductive loop observed in the fourth quadrant was related to two factors, one is the amount of LSCF loading, the other is the testing temperatures. The inductive loop in the impedance spectra disappeared under dc bias or low oxygen partial pressure. Based on this, the inductive loop in the impedance spectra is closely related to the excess oxygen adsorbed on the surface of electrode can be concluded.

1. Introduction

Solid oxide fuel cells (SOFCs) are the most efficient devices for the direction conversion of the chemical energy into electricity [1,2]. Over the past decade, considerable progress has been succeeded in bringing the temperature down to an intermediate and low temperature (ILT), ranging from 400 to 800 °C, so metallic interconnects could be used to reduce the cost. However, decreasing the temperature reduces both electrolyte conductivity and electrode kinetics, resulted in the cell performance. These problems are generally addressed by decreasing the thickness of the electrolyte or developing high performance cathodes and anodes with high electrocatalytic activity for O_2 reduction and direct oxidation of hydrocarbon fuels, respectively [3–5].

Recently, wet impregnation method has been widely studied by introducing nanosized and catalytic active particles into porous scaffolds to form functional composite electrodes of SOFCs, dramatically enhanced their electrochemical performance and avoided the difficulties of thermal expansion mismatch and potential detrimental reactions between electrode and electrolyte. Some researchers [2,6–10] had thoroughly reviewed the progress in the application both in cathodes and anodes, and had discussed the advances and challenges in the development of nanoscale and nano-structure electrode.

We prepared nano-structured composite cathodes such as Pd + YSZ [11,12], LSCF + YSZ [13,14], Pd + LSM [15], LSCN + GDC [16] by impregnation technology. These cathodes are superior to electrocatalytic activity and low activation energy for the O_2 reduction reaction. The electrocatalytic properties are measured by electrochemical impedance spectroscopy (EIS) using a "three-electrode" configuration. However, these electrodes impedance of the three-electrode cell shows a remarkable pseudo-inductive loop in the fourth quadrant at zero dc bias, which is different from the performance of the LSCo-, LSF- and LSM impregnated YSZ nano-structure electrode and $La_{0.4875}Ca_{0.0125}Ce_{0.5}O_{2-\delta}$ impregnated LSCF electrode reported by Huang et al. [17–19] and Liu [20] in a "symmetric two-electrode" configuration. A similar "pseudo-inductive loop" was observed for Ni/$Ce_{0.8}Gd_{0.2}O_{1.9}$ anodes [21] and a direct methanol fuel cell anode [22]. The small inductive loop still was observed in the EIS for the LSCF and LSM electrodes prepared by screen printing method [23,24]. The appearance of inductive loop in EIS decreased frequency to 1 Hz can be related to the adsorption of intermediate species (oxygen ions O^{2-}, O^{-}) in the multistep transfer of oxygen reduction [25,26], without further explanation of the mechanism causing this inductive loop. Boukamp [27] explained the presence of inductive loop at low frequencies in a three-electrode set up by a "crosstalk" between the working electrode and the reference electrode, and the crosstalk is most likely mediated by surface diffusion of charged adsorbed oxygen species. Zhen et al. [28] explained that the significant adsorption of oxygen species on the electrode surface is responsible for the appearance of the low frequency inductance loop according to the mechanism of O_2 reduction on LSM cathodes under dc bias.

A consensus among in the literature review is that the inductive loop is affected by the surface adsorption and diffusion of oxygen species. This paper manages to address the issue that what factors influence the appearance of inductive loop and how to analyze the strong pseudo-inductive loop at low frequency in a three-electrode set up on nano-structure LSCF-YSZ cathode.

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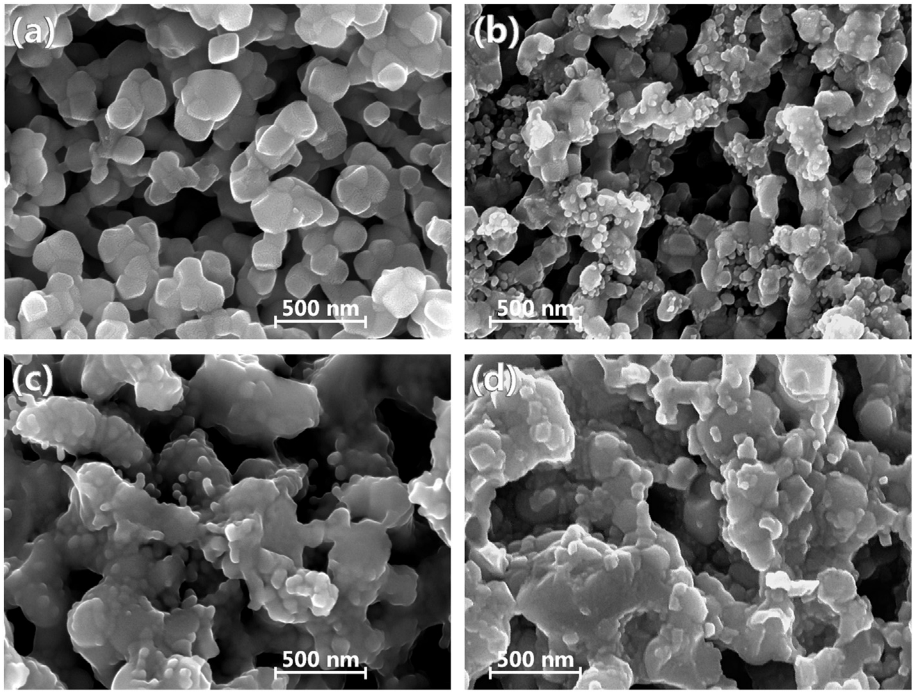

Fig. 1. SEM micrographs of the fractured cross-section of the LSCF impregnated cathodes after EIS testing. (a) 0 wt% of LSCF (b) 12 wt% of LSCF (c) 20 wt% of LSCF, and (d) 28 wt% of LSCF.

2. Experimental

The YSZ electrolyte substrates were prepared by sintering die-pressed disks of 8% mol YSZ powder (TZ-8YS, Tosoh, Japan) at 1500 °C for 4 h in air, followed by mechanical polishing. The substrate disks are 21 mm in diameter and 1.2 mm in thickness. The slurry of 26 nm YSZ (TZ-8Y, Tosoh, Japan) was prepared and applied to the YSZ electrolyte disks by screen printing, followed by sintering at 1200 °C for 1 h in air. The porous YSZ layer on the dense YSZ electrolyte was established with the thickness of 8–10 μm and the active electrode area of 0.5 cm^2.

The $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) impregnation solution was prepared from $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ (Sinopharm Chemical Reagent Co. Ltd) at a molar ratio of La: Sr: Co: Fe = 6:4:2:8, fluorocarbon surfactant, isopropyl alcohol and deionized water. Impregnation was carried out by placing the pre-sintered porous YSZ structure into the LSCF solution under ultrasonic treatment for 10 min. The impregnated samples were dried in the air, and then fired at 800 °C in air for 1 h. The weight gain of the impregnated samples is recorded after firing. LSCF loading is ~0.4 $mg\,cm^{-2}$ for one time impregnation and the process is repeated to increase the LSCF loading. Pt paste was painted on the top of the cathodes as the current collector and on the reverse side of the electrolyte disk formed the counter and reference electrodes. The counter electrode was positioned symmetrically opposite to the working electrode and the reference electrode was painted as a ring at the edge of the electrolyte substrate. Pt mesh was attached to the Pt paste for measuring lead connections. Electrochemical impedance spectra (EIS) are obtained at temperatures at the temperature between 600 and 750 °C on an impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287) at frequency range from 0.1 Hz to 100 kHz with the signal amplitude of 10 mV. EIS measurements were made under open circuit at the measuring temperature in various controlled atmospheres consisted of N_2 and O_2 and under cathodic dc bias conditions. Polarization behavior is studied under a constant current of 200 $mA\,cm^{-2}$ at 750 °C in the air. The total gas flow rate is 100 $mL\,min^{-1}$ with N_2 and O_2 respectively controlled by a mass flow meter.

3. Results and discussion

Fig. 1 illustrates that the SEM images of the LSCF impregnated cathodes on YSC scaffold with different percentage by mass of LSCF. Prior to the impregnation, the YSZ porous layer was well sintered, forming a rigid three-dimensional network with a grain size in the range of 0.2–0.4 μm (Fig. 1a). After 12 wt% of LSCF-impregnation, the nano-sized particles were observed on the surface of porous YSZ grains, and some YSZ electrolyte was exposed to air (Fig. 1b). As the mass of LSCF-impregnation increased to 20 wt%, there is significant increased coverage of nanoparticles on the YSZ grains, and the YSZ substrate is covered with layers of LSCF particles (Fig. 1c). As the impregnation added up to 28 wt%, some fine pores of the original YSZ porous structure were filled by nanoparticles and there is formation of a continuous and porous network of LSCF-YSZ phase (Fig. 1d).

Fig. 2 shows the electrochemical impedance spectra (EIS) of the impregnated LSCF-YSZ composed of various loadings with the measured temperature ranging from 600 to 750 °C. In this figure, x wt% is the percentage by mass of LSCF and YSZ scaffold. Electrodes with the value of x are 12, 18, 20, 28 and 32 are prepared respectively. When increased the LSCF loading on the YSZ scaffold, the impedance spectra have a great change. For example, in Fig. 2 the impedance spectra of the LSCF-YSZ electrode with 12 wt% LSCF is a depressed arc in the first quadrant. The 1000 Hz frequency response point appeared at the central of the impedance spectra, and 100 Hz frequency response point appeared at the end of the impedance spectra. The oversize of the impedance arcs decreased with increasing LSCF content x to 18. Prior reports suggests that to fit in the spectra using a nonlinear least squares, two arcs or even three arcs were observed which called high- and low-frequency arcs. Significant overlap was observed between the arcs, giving the appearance of a single depressed arc [29]. When the LSCF loading reached 18 wt%, there is a significant inductive loop appeared in the fourth quadrant. The impedance spectra are consisted of two parts. One part is the capacitive arc in the first quadrant with 1000 Hz frequency response point appeared at the central of the capacitive arc and the other is the inductive loop in the fourth quadrant with 100 Hz frequency response point. Increasing LSCF content x to 28 and 32, the