



High performance transition metal oxide composite cathode for low temperature solid oxide fuel cells

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ABSTRACT

Low temperature solid oxide fuel cells (SOFCs) with metal oxide composite cathode on the ceria–carbonate composite electrolyte have shown promising performance. However, the role of individual elements or compound is seldom investigated. We report here the effect of the ZnO on the physico-chemical and electrochemical properties of lithiated NiO cathode. The materials and single cells are characterized by X-ray diffraction, scanning electron microscopy, DC polarization electrical conductivity, electrochemical impedance spectroscopy and fuel cell performance. The ZnO modified lithiated NiO composite materials exhibit smaller particle size and lower electrical conductivity than lithiated NiO. However, improved electro-catalytic oxygen reduction activity and power output are achieved after the ZnO modification. A maximum power density of 808 mW cm^{-2} and the corresponding interfacial polarization resistance of $0.22 \Omega \text{ cm}^2$ are obtained at 550°C using ZnO modified cathode and $300 \mu\text{m}$ thick composite electrolyte. The single cell keeps reasonable stability over 300 min at 500°C . Thus, ZnO modified lithiated NiO is a promising cathode candidate for low temperature SOFCs.

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1. Introduction

Solid oxide fuel cells are of technological interest because of their high-energy conversion efficiency, excellent fuel flexibility and minimal pollutant emission [1,2]. Great efforts have been made in the past decades to lower the operational temperature to reduce the cost and component degradation. Electrolyte material is a key component for SOFCs, which determines the working temperature, largely. So far, the major work has been focused on single phase materials, such as doped ceria, doped LaGaO_3 perovskite and BaCeO_3 based perovskite proton conductor, to replace the conventional YSZ electrolyte. However, these materials still suffer one or more disadvantages that hinder their practical uses. For example, electronic conductivity of doped ceria in the reduced atmosphere leading to lower fuel efficiency [3] and high reactivity of LSGM causing the materials instability [4]. More importantly, the ionic conductivities of these materials are still much lower than the target values of 0.1 S cm^{-1} in order to deliver high power outputs at 600°C .

In parallel, extensive research activities on ceria–carbonate composite have shown that ceria–carbonate composites are potential electrolyte materials for low temperature SOFCs ($300\text{--}600^\circ\text{C}$) [5–14]. The composite electrolytes possess extreme high conductivity [7,9] and show a mixed proton and oxygen ionic conductive property under fuel cell condition [11]. These two reasons lead to a maximum power density of ca. 1.15 W cm^{-2} at 500°C reported by Raza et al. [10]. More recent study showed the ionic conductivity of ceria–carbonate composite is stable in air over 1500 h [13]; and single cell using composite electrolyte and optimized electrodes presented stable performance in 100 h non-stop measurement [14]. These achievements have further promoted the ceria–carbonate composites as the competitive electrolytes for low temperature SOFCs.

For most studies on the ceria–carbonate composite electrolyte based SOFCs, the practical cathode materials are lithiated NiO. Number of studies has proved its sufficient activity for oxygen reduction reaction (ORR) under fuel cell conditions [8–11]. However, the gradual dissolution of lithiated NiO into the molten carbonate will cause progressive deterioration of material and cell performance [15,16]. Therefore, alternative cathodes have been explored to solve or relieve this challenging issue [14,17–19]. For example, Zhang et al. [14] employed $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ as cathode and reported that a stable performance was obtained

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during a nonstop 100 h measurement. However, the cell performances with these materials are much worse than those with conventional lithiated NiO cathode.

Recently, a series of functional transition metal oxide composite based on the NANOCOFC (nano-composites for advanced fuel cell technology) concept was developed and evaluated as novel electrodes for SOFCs at low temperatures. The electrode materials are composited by metal transition oxide, such as Fe_2O_3 , NiO, CuO, SrO and ZnO. Superior performances have been achieved with these composite electrodes [20–25]. However, previous researches are focused on the fuel cell performance, the role of the individual element or compound is seldom studied and identified. In this work, we intentionally choose a ZnO modified lithiated NiO composite oxide for its high cathode activity on the ceria-carbonate composite electrolyte. The influences of ZnO modification on the crystal structure, morphology, electrical conductivity and electrochemical properties of the composite cathode for low temperature SOFCs are examined experimentally. The short-term stability test is also carried out.

2. Experimental

ZnO modified lithiated NiO was synthesized by solid-state reaction using LiOH, $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$ and ZnCO_3 as the raw materials. The transition metal salts were preheated at 600°C for 2 h to get the oxides (NiO and ZnO). Then stoichiometric numbers of oxide and LiOH were blended thorough with pestle and mortar. The molar ratio of Li:Ni:Zn was 1:2:2. The mixtures were subsequently sintered at 700°C for 3 h. After cooled down to room temperature, the blank powders were pulverized for further use. Lithiated NiO was prepared by mixing LiOH and NiO with a molar ratio of 1:1 and subsequently sintered at 700°C for 3 h. NiO was used as the anode catalyst.

Ceria-carbonate electrolyte composed of 80 wt.% samarium doped ceria (SDC) and 20 wt.% $(\text{Li}/\text{Na})_2\text{CO}_3$ was prepared according to the procedure described previously [11]. Composite electrodes were the mixture of the above catalysts and composite electrolyte in the weight ratio of 1.5:1.

To test the electrical conductivity of lithiated NiO and ZnO modified lithiated NiO, pellets were prepared by dry-pressing with a diameter of 13 mm and a thickness of 2 mm and sintered at 650°C to achieve sufficient mechanical strength. The electrical conductivity was measured by a standard DC four-probe technique on the Digital Micro-ohmmeter (KD 2531, Shanghai, China) between 600°C and 200°C in air. The crystal structures of the samples were characterized using a Philips X'pert pro super Diffractometer (XRD). The powder morphologies and compositions as well as the fuel cell microstructures were examined using scanning electron microscope (SEM, Zeiss, Germany), coupled with energy-dispersive X-ray spectroscopy (EDS) unit for elemental analysis.

Electrolyte supported SOFCs (both for symmetrical cells and complete single cells) were prepared by one step uniaxial dry-pressing using a load of 300 MPa into pellet in a configuration, electrode | composite electrolyte | electrode, as reported before [12]. *I*-*V* data were recorded by a fuel cell tester (SM-102, Sanmu Co., China) under different resistance loading. Hydrogen was fed into anode chamber at flow rate of $100\text{--}120\text{ ml min}^{-1}$. AC impedance spectra were measured by an impedance analyzer VERASTA 4 (Princeton Applied Research, USA) under open circuit condition at different temperatures ($500\text{--}600^\circ\text{C}$). The applied frequency range is 0.1 Hz–100 kHz with an excitation amplitude of 20 mV. The spectra curve fitting was performed using the ZSimpWin Software (Princeton Applied Research, USA). All data were collected in 30 min after the desired temperature was reached.

3. Results and discussion

Fig. 1 shows the XRD profiles of lithiated NiO and ZnO modified lithiated NiO. It can be seen that the diffraction peaks of lithiated NiO are higher than those of ZnO modified sample, suggesting that higher crystallization was achieved for lithiated NiO powder after thermal treatment. All peaks of the lithiated NiO are well fitted to $\text{Li}_{0.68}\text{Ni}_{1.32}\text{O}_2$ (JCPDS:88-1605). While for ZnO modified oxide, peaks belonged to ZnO (JCPDS:89-0511) are also detected except the crystal phase of lithiated NiO ($\text{Li}_{0.4}\text{Ni}_{1.6}\text{O}_2$, JCPDS:81-0095). The peaks positions of $\text{Li}_{0.4}\text{Ni}_{1.6}\text{O}_2$ shift slightly to low angle, which could be interpreted by the small amount of Zn doping in the lithiated NiO lattice (up to 10 mol% [26]) because the ionic radius of Ni^{2+} (0.069 nm) is smaller than Zn^{2+} (0.074 nm). Besides, one unknown small crystal peak ($2\theta = 25\text{--}26^\circ$) also appears in the ZnO modified sample. Therefore, the ZnO modified sample is mainly constituted by the individual metal oxide and lithiated nickel oxide, which is consistent with previous reports [22–24]. The SEM images (Fig. 2a and b) show that the ZnO modified oxide composite exhibits smaller particle size and more homogeneous size distribution than ZnO free one. The mean particle sizes are 150 nm and 300 nm for ZnO modified sample and lithiated NiO, respectively. It can be deduced that the modification with ZnO can restrain the particle growth of lithiated NiO. Simultaneously, the smaller particle size would offer more active sites for electrochemical reaction, and thus, enhance the fuel cell performance. In light of the selected area EDS results of ZnO modified or not modified samples, as displayed in Fig. 2, respectively, the powders are made up of nickel, oxygen and/or Zn atom, ruling out incorporation of any additional impurities during the sample preparation (Al was used as the sample holder). It should be noticed that Li cannot be detected by EDS. The recorded atom ratio of Ni and Zn in the composite slightly departs from the theoretical value, which may be the results of inadequate solid state reaction time and reaction temperature.

Sufficient electrical conductivity of electrode materials could ensure good current collection and power output. Thus the electrical conductivity measurements were performed in air using the DC four-probe technique, and the results are shown in Fig. 3. It should be noted that the lithiated metal oxides cannot be fully dense because of the volatilization of Li_2O at the elevated temperature [27]. Sample sintered at 650°C can reveal the in situ electrical conductivity. The conductivities of all samples gradually increase with the increase of temperatures. The $\ln(\sigma T)$ shows a linear relationship to $1000/T$, indicating that the electrical

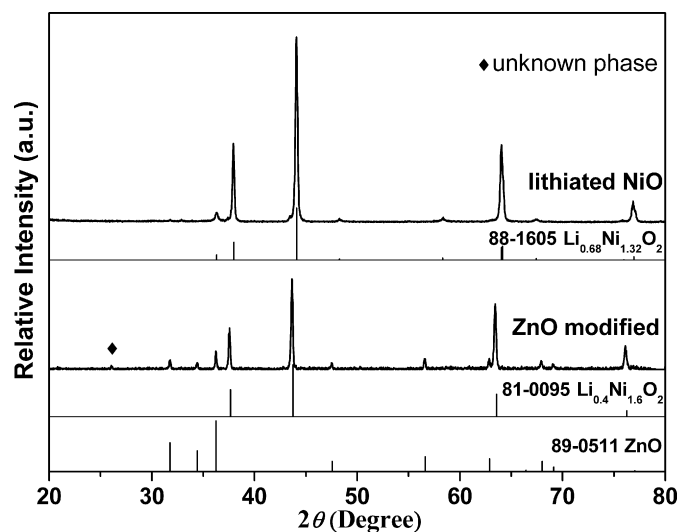


Fig. 1. XRD patterns of lithiated NiO [12] and ZnO modified lithiated NiO.

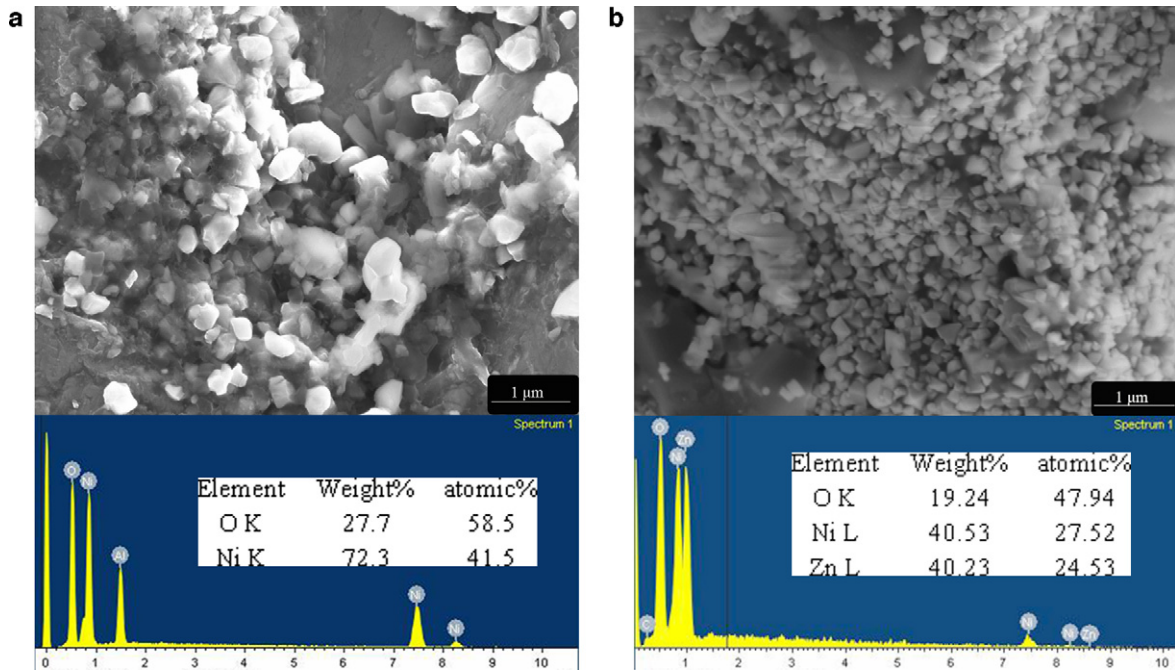


Fig. 2. SEM images of (a) lithiated NiO and (b) ZnO modified lithiated NiO and their corresponding EDS spectra analysis.

conductivity behavior follows the small polaron conductivity mechanism. The conductivity of lithiated NiO is 12.0 S cm^{-1} at 600°C , which is consistent with the previous report [28]. Compared with lithiated NiO, the conductivity of ZnO modified sample is reduced, only 3.2 S cm^{-1} at 600°C , which may be attributed to the electronic block effect of ZnO in a constant oxidation state and the possible reduced conductivity by the partial doping of Li into ZnO lattice [29,30]. Although the electrical conductivities of these samples are far from the standard value of 100 S cm^{-1} [31], and they may be further reduced when composited with electrolyte, good performance is still manageable when two aspects are taken into account. One is that the electronic and ionic conductivities in a well matched condition for these composites, which together determine the final cathode performance to deliver current and power output for the fuel cell [25]. The other is that a suitable current collector can be adopted. Indeed, some novel cathode materials for SOFCs with

low electrical conductivity still showed satisfactory performance. For example, the electrical conductivity of the cathode alternative-double perovskite $\text{NdBaCo}_2\text{O}_{5+\delta}$ is 10 S cm^{-1} and the Co site Fe doped $\text{NdBaCo}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$ is only 1 S cm^{-1} . The maximum power densities, however, are 0.866 and 1.034 W cm^{-2} at 1023 K , respectively, when Ag paste was employed as current collector [32]. In addition, the calculated activation energies are 0.108 and 0.205 eV for lithiated NiO and ZnO modified cathode, respectively.

Impedance measurements were performed on symmetrical cells with the composite electrode in both sides to study the electrochemical behavior of cathode on ceria–carbonate electrolyte. Fig. 4a and b shows the impedance spectra of the symmetrical cells with lithiated NiO and ZnO modified cathode, respectively. To demonstrate clearly the difference in electrode polarization behavior, all bulk resistances are removed from the impedance data. As can be seen, all the impedance spectra are characterized by the presence of one high frequency loop and an extension at low frequency, indicating that at least two different electrode processes for the ORR. The high frequency loop is related to the charge transfer process. Alternatively, the low frequency extension or tail is corresponded to mass diffusion process [33,34]. The catalytic activity of electrode is major determined by the charge transfer process. In order to get the more accurate values of the different processes, the impedance spectra were modeled with an equivalent circuit of $L - (R_1 QPE_1) - (R_2 QPE_2)$ using a Zsimpwin software as shown the inset of Fig. 4c. In the equivalent circuit, L denotes an inductance element arising from the stainless steel reactor and instrument leads, R_1 is charge transfer resistance and R_2 is the gas diffusion resistance, and QPE is constant phase element. A typical fitting result for the ZnO modified cathode cells at 600°C is also displayed. The fitted R_1 values for different electrodes are shown in Table 1. In general,

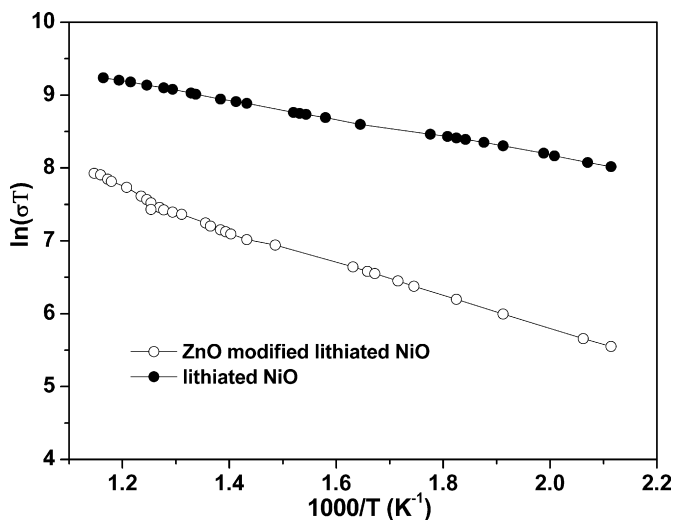


Fig. 3. Electrical conductivity of lithiated NiO and Zn modified electrode at different temperatures.

Table 1

The fitted charge transfer resistance of lithiated NiO and Zn modified electrodes at different temperatures.

	600 °C	550 °C	500 °C
Lithiated NiO	0.56	0.97	2.06
Zn modified lithiated NiO	0.30	0.61	2.69

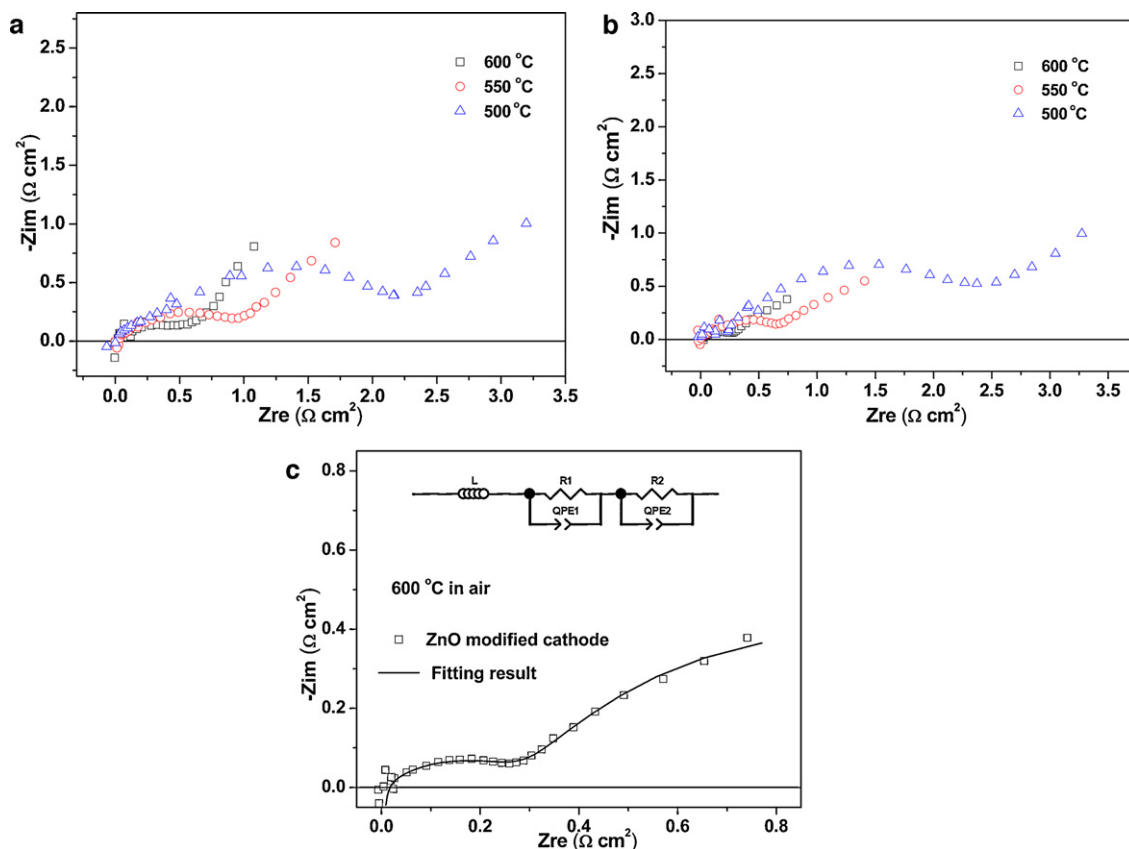


Fig. 4. Electrochemical impedance plots of symmetrical cells with (a) lithiated NiO electrode, (b) ZnO modified electrode measured in air at different temperatures. And (c) a typical fitting result of ZnO modified cathode symmetrical cell at 600 °C with the applied equivalent circuit model of $L(R_1QPE_1)(R_2QPE_2)$ shown as an inset.

R_1 values decrease with the increase of operational temperature for both samples. As can be seen in Table 1, the charge transfer resistances of the ZnO modified electrode show the lower values than those of unmodified electrode at 550 and 600 °C, exhibiting 0.61 Ω cm² and 0.97 Ω cm² at 550 °C, respectively. The high catalytic activity of ZnO might contribute the comparable electrochemical performance though the total electrical conductivity is lower [35]. Besides, positive contribution onto the improved triple phase boundaries due to the reduced particle size is also accounted for the enhanced performance. In addition, the polarization resistances at those temperatures are still higher than 0.15 S cm² [36]. But it should be pointed out that these values would be significantly reduced in the fuel cell condition, or especially under DC polarization condition [37]. Finally, the electrode microstructures

are needed to optimize because the mass diffusion resistance will also cause big loss as shown in the low frequency tail of the Nyquist plots.

To further study the electrochemical properties of the ZnO modified lithiated NiO cathode in fuel cell condition, complete fuel cells were fabricated and characterized by current density–voltage and current density–power density (I – V & I – P) characteristics and electrochemical impedance spectra. The results are displayed in Figs. 5 and 6. Fig. 5a shows that polarization curves of fuel cells with different cathodes at 550 °C. The open circuit voltage (OCV) values were 0.97 V for lithiated NiO and 0.94 V for ZnO modified samples, somehow lower than the theoretic thermodynamically values by Nernst equation. Gas crossover through the composite electrolyte due to the cold powder compacting and low sintering temperature

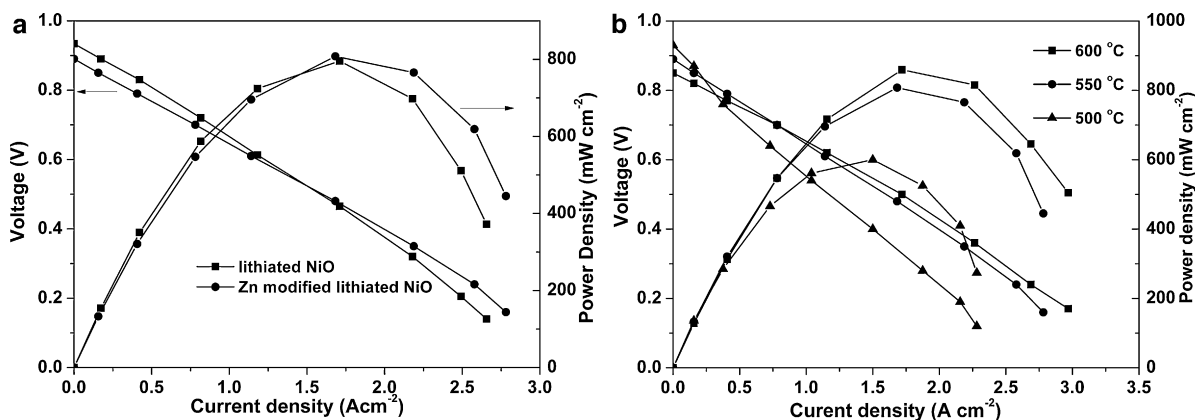


Fig. 5. Electrochemical performances of single cells with (a) different cathode materials at 550 °C and (b) Zn modified cathode at different temperatures.

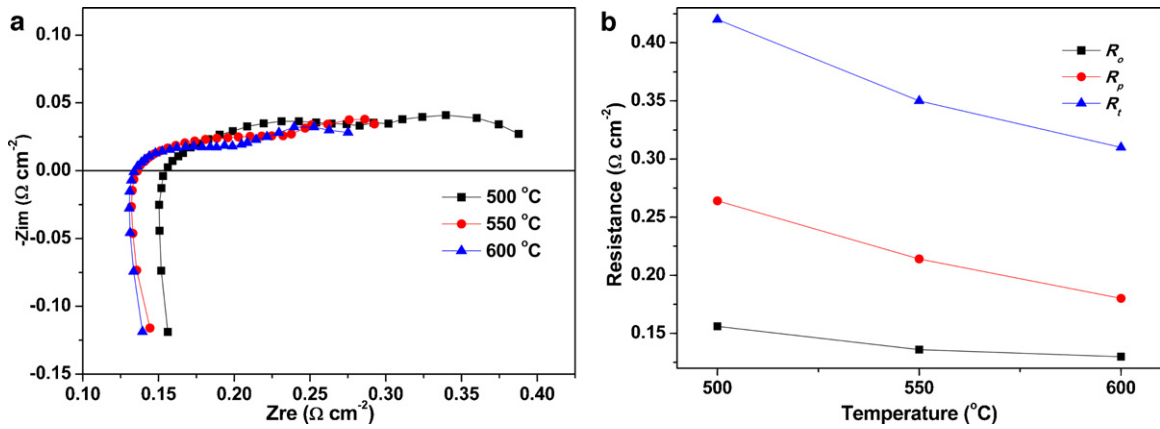


Fig. 6. (a) Typical electrochemical impedance spectra of single cells with ZnO modified cathode at 600, 550 and 500 °C under OCV conditions and (b) the electrode polarization resistance, electrolyte resistance and total resistance contribution derived from the impedance spectra.

(600 °C), which could leave residual pores, would result in such low OCV values. The OCV value of single cell using ZnO modified cathode is lower than that using the lithiated NiO cathode. However, the maximum power density of single cells using the ZnO modified cathode (808 mW cm^{-2} at 550 °C) is better than that of using the unmodified cathode (795 mW cm^{-2}). Performance of the single cell using ZnO modified cathode at various temperatures is also shown in Fig. 5b, reaching maximum power densities of 859, 808 and 600 mW cm^{-2} at 600, 550 and 500 °C, respectively. The performances reported here are comparable to that reported by Wang et al. [9] using lithiated NiO cathode, but higher than the values reported by Zhang et al. [14] using $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ cathode and Gao et al. [19] with $\text{La}_{1-x}\text{Sr}_x\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ cathode based on the same fuel cell configuration and the similar ceria-carbonate electrolytes. Therefore, it may be concluded that the ZnO modified lithiated NiO cathode shows acceptable electro-catalytic activity for ORR.

The polarization behavior of the fuel cells, recorded by AC impedance spectroscopy at different temperatures under open-circuit conditions, is displayed in Fig. 6a. The high frequency intercept corresponds to overall ohmic area specific resistance (R_o) of the cell, including charge transport resistance of the electrolyte and electrodes and contact resistance associated with interfaces, while the low frequency intercept corresponds to the total area specific resistance (R_t). Therefore, the difference between the high frequency and low frequency intercepts on the real axis represents the total interfacial polarization area specific resistance (R_p) of the cell [38]. The R_o values are 0.13, 0.14 and $0.16 \Omega \text{ cm}^2$ at 600, 550 and 500 °C, respectively. Considering that the electrolyte ohmic area specific resistance occupies major part of the R_o , the corresponding DC conductivities (σ) of the used composite electrolyte are 0.23, 0.21 and 0.19 S cm^{-1} , respectively. They are calculated from equation: $\sigma = L/R_o(A)$, in which L is the thickness of the electrolyte. The excellent conductivity demonstrated again that the ceria-carbonate composite is a promising functional electrolyte for low temperature SOFCs. As expected, the increase of the measurement temperature results in an effectively decline of the total resistances and interfacial polarization resistance (see Fig. 6b), typically from 0.42 and $0.26 \Omega \text{ cm}^2$ at 500 °C to 0.31 and $0.18 \Omega \text{ cm}^2$ at 600 °C, respectively. Besides, it can be seen that the interfacial polarization resistances are higher than the ohmic resistances at the whole working temperature range. For instance, the total resistance of the cell is $0.31 \Omega \text{ cm}^2$ while the R_p accounts for only 58% of the total cell resistance at 600 °C. Therefore, the cell performance is essentially determined by the interfacial polarization resistance, which agrees well with the electrode materials study trends [39].

Compared with the polarization resistance of the ZnO modified electrode in symmetrical fuel cell measured above in air, see Fig. 4, the cathode/electrolyte interfacial polarization resistance is substantially reduced in fuel cell condition. As can be seen in Fig. 6a, there are two depressed arcs contained in the fuel cell impedance spectra. Generally, the low frequency arc is related to the cathode/electrolyte interfacial reaction and the high frequency arc is concerned to the anode/electrolyte interfacial reaction [40,41]. At the whole operational temperature range, the low frequency arcs show similar diameters with the high frequency arcs, suggesting that the ORR kinetics in ZnO modified lithiated NiO cathode is close to the hydrogen oxidation reaction kinetics in Ni anode, again demonstrating its adequate electrochemical activity at this operational temperature range. The area specific charging transfer resistance at 550 °C is $0.61 \Omega \text{ cm}^2$ in air, while the cathodic interfacial resistance is only around $0.11 \Omega \text{ cm}^2$. This significantly reduced polarization resistance may be explained: (i) the ceria-carbonate composite electrolyte as reported show a hybrid proton and oxygen ionic conductive property [11,12]. In some case, the proton conduction may predominate the total ionic transportation [42], while the introduction of proton conduction would promote the kinetics of electrode and interfacial reaction [5]; (ii) previous work showed that proton can transport in the layered oxide resulting in higher cathode catalysis [43]; (iii) the electrical conductivity of the hydrogen-implanted ZnO increases by four orders of magnitude [29], which may effectively decrease the cathode polarization losses. All of them effectively promote the

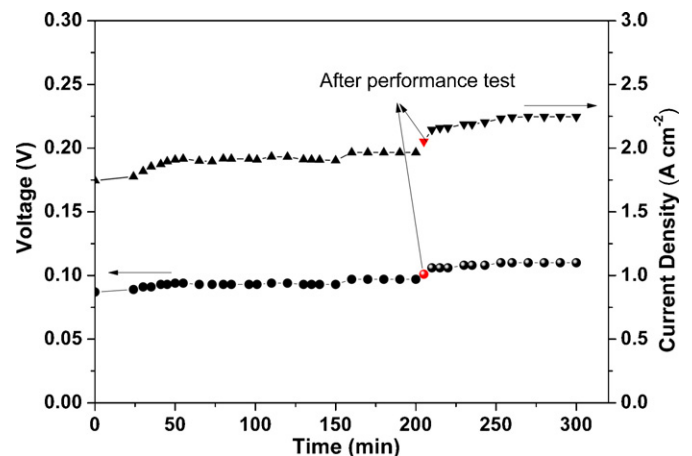


Fig. 7. Stability test of single cell using Zn modified cathode under a constant resistance at 500 °C.

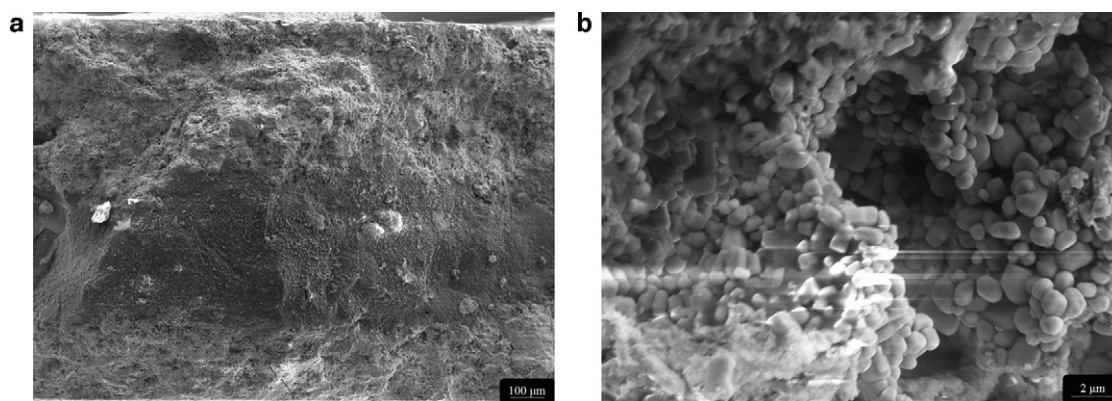


Fig. 8. SEM images of the fractural cross-section of single cell with Zn modified cathode after stability test: (a) the whole cell and (b) composite cathode.

cathode/electrolyte interfacial kinetics for ORR, but the clarification of the detailed mechanism requires further studies by more convective experiments.

Fig. 7 shows the short-term stability measurement for the fuel cells with ZnO modified lithiated NiO cathode. The fuel cell performed at the minimum resistance, almost close to a short circuit condition by delivering a beginning current density of 1.9 A cm^{-2} . The voltage and current density responses are reasonably stable for an initial test period of 200 min at 500°C , while fuel cell with lithiated NiO cathode and the similar electrolyte decreased quickly during the first 200 min durability test [16], where the obvious morphology change at cathode/electrolyte interface caused by the dissolution of Ni ion conducted to the degradation. In fact, Huang et al. [26] reported that the ZnO additive has a strong positive effect on the reduction of NiO solubility in carbonate melts. It is worth to note that, after the fuel cell operation was intermittently stopped for OCV and I - V performance measurements, the maximum current density was improved from 1.90 A cm^{-2} to 2.25 A cm^{-2} . The observed fuel cell OCV is also enhanced relative to before testing from 0.97 V to 1.00 V . These results suggest that the electrode/electrolyte interface and the microstructure of composite electrolyte can be continuously activated during the operation. The fuel cell was then operated steadily for the rest 100 min. Therefore, one could assert that the ZnO modified lithiated NiO cathode can keep essentially stable at fuel cell condition and show reliable bonding with ceria-carbonate composite electrolyte with reduced polarization losses. Although the result is encouraging, more extended long-term stability testing is obviously needed in future work, taking into account its great importance in practical interest.

Fig. 8a and b shows the SEM images of the cross sections of single cell after the stability tests. The cell preserves good geometric integrity without any delimitation or crack between respective layers after stability test. A good bond between electrolyte and electrodes will ensure high fuel cell performance as a result of the effectively improved interfacial properties. In fact, the interfacial thermal stress has been significantly reduced at lower temperature compared to high working temperature (above 600°C). In addition, the existing of carbonate in our system may act as lubricants to adjust the interfacial thermal stress difference. Also, an idea cathode microstructure (moderate porosity and well-necked particles) is observed, see Fig. 8b, which will supply convenient channels for rapid gas phase and charge transport in cathodic electrochemical process. Therefore, the excellent performance is also ascribed to the optimized cathode microstructure and well bonded interfaces.

4. Conclusions

In summary, lithiated NiO was modified by ZnO and applied as cathode for low temperature SOFCs with ceria-carbonate

composite electrolyte and its performance was evaluated by various techniques. Though the electrical conductivity of Zn modified lithiated NiO is low, the oxygen reduction capability and fuel cell performance are similar to or even better than those of lithiated NiO because of the improved oxygen reduction activity and reduced particle size. A maximum power density of 808 mW cm^{-2} was achieved at 550°C . Stable performance was proved over a 300 min duration test. All results suggested that ZnO modified lithiated NiO composite is a potential cathode material for ceria-carbonate composite electrolyte based SOFCs. Results presented here also indicate that NANOCOFC approach is a prospective solution to explore the super-performance electrode materials and advanced generation for low temperature SOFCs.

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References

- [1] B. Steele, *J. Power Sources* 49 (1994) 1–14.
- [2] A. Atkinson, S. Barnett, R. Gorte, J. Irvine, A. McEvoy, M. Mogensen, S. Singhal, J. Vohs, *Nat. Mater.* 3 (2004) 17–27.
- [3] X. Zhang, M. Robertson, C. Deces-Petit, W. Qu, O. Kesler, R. Maric, D. Ghosh, *J. Power Sources* 164 (2007) 668–677.
- [4] P. Huang, A. Horky, A. Petric, *J. Am. Ceram. Soc.* 82 (1999) 2402–2406.
- [5] B. Zhu, X. Liu, P. Zhou, X. Yang, Z. Zhu, W. Zhu, *Electrochem. Commun.* 3 (2001) 566–571.
- [6] B. Zhu, *J. Power Sources* 114 (2003) 1–9.
- [7] B. Zhu, X. Yang, J. Xu, Z. Zhu, S. Ji, M. Sun, J. Sun, *J. Power Sources* 118 (2003) 47–53.
- [8] J. Huang, Z. Mao, Z. Liu, C. Wang, *Electrochem. Commun.* 9 (2007) 2601–2605.
- [9] X. Wang, Y. Ma, R. Raza, M. Muhammed, B. Zhu, *Electrochem. Commun.* 10 (2008) 1617–1620.
- [10] R. Raza, X. Wang, Y. Ma, X. Liu, B. Zhu, *Int. J. Hydrogen Energy* 35 (2010) 2684–2688.
- [11] J. Di, M. Chen, C. Wang, J. Zheng, L. Fan, B. Zhu, *J. Power Sources* 195 (2010) 4695–4699.
- [12] L. Fan, C. Wang, M. Chen, J. Di, J. Zheng, B. Zhu, *Int. J. Hydrogen Energy* 36 (2011) 9987–9993.
- [13] M. Benamira, A. Ringuedé, V. Albin, R. Vannier, L. Hildebrandt, C. Lagergren, M. Cassir, *J. Power Sources* 196 (2011) 5546–5554.
- [14] L. Zhang, R. Lan, A. Kraft, S. Tao, *Electrochem. Commun.* 13 (2011) 582–585.
- [15] L. Giorgi, M. Carewska, M. Patriarca, S. Scaccia, E. Simonetti, A. Di Bartolomeo, *J. Power Sources* 49 (1994) 227–243.
- [16] L. Zhang, R. Lan, C.T.G. Petit, S. Tao, *Int. J. Hydrogen Energy* 35 (2010) 6934–6940.
- [17] S. Li, J.C. Sun, X.L. Sun, B. Zhu, *Electrochem. Solid State Lett.* 9 (2006) A86–A87.
- [18] J. Huang, R. Gao, Z. Mao, J. Feng, *Int. J. Hydrogen Energy* 35 (2010) 2657–2662.
- [19] Z. Gao, Z. Mao, C. Wang, Z. Liu, *Int. J. Hydrogen Energy* 35 (2010) 12905–12910.
- [20] M.D. Mat, X. Liu, Z. Zhu, B. Zhu, *Int. J. Hydrogen Energy* 32 (2007) 796–801.
- [21] R. Raza, X. Wang, Y. Ma, B. Zhu, *J. Power Sources* 195 (2010) 8067–8070.

- [22] B. Zhu, R. Raza, H. Qin, Q. Liu, L. Fan, *Energy Environ. Sci.* 4 (2011) 2986–2992.
- [23] B. Zhu, R. Raza, H. Qin, L. Fan, *J. Power Sources* 196 (2011) 6362–6365.
- [24] B. Zhu, R. Raza, G. Abbas, M. Singh, *Adv. Funct. Mater.* 21 (2011) 2465–2469.
- [25] B. Zhu, H. Qin, R. Raza, Q. Liu, L. Fan, J. Patakangas, P. Lund, *Int. J. Hydrogen Energy* 36 (2011) 8536–8541.
- [26] B. Huang, F. Li, Q. Yu, G. Chen, B. Zhao, K. Hu, *J. Power Sources* 128 (2004) 135–144.
- [27] T. Sata, *Ceram. Int.* 24 (1998) 53–59.
- [28] C. Yuh, J. Selman, *J. Electrochem. Soc.* 138 (1991) 3642–3648.
- [29] Z. Zhou, K. Kato, T. Komaki, M. Yoshino, H. Yukawa, M. Morinaga, K. Morita, *J. Eur. Ceram. Soc.* 24 (2004) 139–146.
- [30] J. Park, J. Zou, H. Yoon, G. Kim, J.S. Chung, *Int. J. Hydrogen Energy* 36 (2011) 6184–6193.
- [31] S. McIntosh, R. Gorte, *Chem. Rev.* 104 (2004) 4845–4865.
- [32] S. Yoo, J.Y. Shin, G. Kim, *J. Electrochem. Soc.* 158 (2011) B632–B638.
- [33] I. Uchida, T. Nishina, Y. Mugikura, K. Itaya, *J. Electroanal. Chem. Interfacial Electrochem.* 206 (1986) 229–239.
- [34] S. Adler, X. Chen, J. Wilson, *J. Catal.* 245 (2007) 91–109.
- [35] H. Park, S. Kim, *Electrochem. Solid State Lett.* 10 (2007) B187–B190.
- [36] B. Steele, *Solid State Ionics* 86–88 (1996) 1223–1234.
- [37] F. Baumann, J. Fleig, M. Konuma, U. Starke, H. Habermeier, J. Maier, *J. Electrochem. Soc.* 152 (2005) A2074–A2079.
- [38] S. Jiang, J. Love, Y. Ramprakash, *J. Power Sources* 110 (2002) 201–208.
- [39] E. Tsipis, V. Kharton, *J. Solid State Electrochem.* 12 (2008) 1367–1391.
- [40] M. Brown, S. Primdahl, M. Mogensen, *J. Electrochem. Soc.* 147 (2000) 475–485.
- [41] S. Bebelis, S. Neophytides, *Solid State Ionics* 152–153 (2002) 447–453.
- [42] J. Huang, Z. Mao, Z. Liu, C. Wang, *J. Power Sources* 175 (2008) 238–243.
- [43] S. Tao, Q. Wu, Z. Zhan, G. Meng, *Solid State Ionics* 124 (1999) 53–59.