研究简报

CHARACTERISTICS OF NEW CATHODE MATERIAL FOR LTSOFC INVESTIGATED BY IMPEDANCE SPECTROSCOPY

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Abstract The characteristics of a new Li-NiO cathode were investigated. The crystal structure of Li-NiO was explored by XRD. Electrochemical behaviors of Li-NiO composite cathode were revealed by impedance spectroscopy from 400 ℃ to 650 ℃. The diameter of deformed arc increased with the decrease of temperature. Above the melting point of the eutectic salt in composite electrolyte, the Li-NiO curves are similar with two deformed semicircular arcs at high frequency which partially overlaps each other and corresponds to the two electrochemical reactions. The composition of the cathode and its effect on the properties of Li-NiO were also investigated. The interfacial resistances of cathode/electrolyte were studied.

Keywords cathode, LTSOFC, lithiumed nickel oxide

1 INTRODUCTION

Developing low temperature solid oxide fuel cell (LTSOFC, 400—800 ℃) is the most promising work to promote the commercialization of SOFC, by which the cost of SOFC could be largely cut short and complex material problems could be avoided. Among all the efforts, to explore new electrolyte materials with higher ionic conductivity at intermediate temperature. A new type of composite electrolyte, such as doped ceria (DCO)-$LiCl$-$SrCl_2$, was adopted and demonstrated with the peak power density of 510 mW · cm^{-2} at 625 ℃ for SOFC[1—4]. Investigated by the impedance spectroscopy, it was found that the main obstacle might come from the low performance of cathode materials, since the new electrolytes possess such high ionic conductivity about 3—10 times larger than pure DCO at low temperature[1]. It has also been demonstrated that the resistances and the polarization resistances of electrode/ electrolyte interfaces increase dramatically as reducing the operating temperature of SOFC, especially the resistances to oxygen reduction at the cathode. Therefore, optimization of cathode materials and performance is quite essential.

Nickel oxide is the common cathode material of molten carbonate fuel cell, yet it was reported that the diffusing of Li^+ ions from the electrolyte into the nickel oxide could significantly increase the electronic conductivity of the cathode[5,6]. In this paper, new cathode material of lithiumed nickel oxide is proposed for the candidate cathode of LTSOFC, and investigated by electrochemical impedance spectroscopy. The oxygen reduction mechanism at the cathode-electrolyte interface was studied and the structure and composition of cathode material and their effect on the performance of LTSOFC were analyzed.

2 EXPEIMENTAL

LiCl and KCl were mixed in the molar ratio of 58 : 42, and heated at 500 ℃ in air for 30 min to an eutectic salt following a suddenly cooling to room temperature. Blend the eutectic salt and SDC in the salt - mass ratio of 2 0 % sufficiently , and then

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calcine at 550 ℃ in air for 1 h, and the composite electrolyte (noted as CSLK) was achieved.

A new cathode material of lithiumed nickel oxide (Li-NiO) was prepared by blending alkaline nickel carbonate with lithium salt and calcining it at 680 ℃. The composite cathode was achieved by blending Li-NiO with CSLK at the mass ratio of 30 : 70, 40 : 60, 50 : 50 and 60 : 40. The sandwich assembly of cathode/electrolyte/cathode was achieved by uniaxialy cold pressed at 250 MPa and sintered at 650 ℃ for 30 min for the investigation of interface reaction.

X-ray diffraction (D8 diffractometer, Bruker cop. Germany) was used to confirm the crystalline structure of the Li-NiO. The morphology of the powders was examined with scanning electron microscope (SEM, JSM-6301F). The interfacial resistance of cathode and electrolyte was investigated by A. C. impedance from 400 ℃ to 650 ℃ by PerkinElmer 5210 frequency response analyzer (0. 5~120 kHz) combined with EG & G PAR potentiostat/ galvanostat 263 A.

3 RESULTS AND DISCUSSION

3. 1 Powder characteristic

Fig. 1 presents the XRD spectrum of Li-NiO and the standard spectrum of NiO is also shown in contrast. It could be clearly seen that the spectrum of Li-NiO was consistent with the standard NiO, and no other peak was detected. During the preparation of Li-NiO, the calcining temperature is close to the melting point of lithium salt, and the lithium salt was in highly disorder status. With the suddenly cooling procedure, the disorder status was kept in the room temperature, resulting in the disappearance of the spectrum for lithium salt.

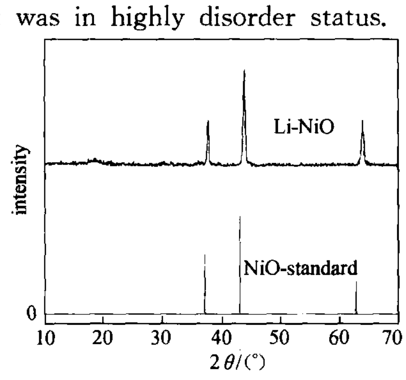

Fig. 1 XRD spectra for Li-NiO powders

3. 2 Electrochemical characterization

Supported by the detection of water at both electrode, the composite electrolyte is deemed to possess both proton and oxygen ionic conductivity. Thus the cathode is not only the area for oxygen reduction, but also for production of water. Fig. 2 presents the Nyquist diagram of the composite cathode with the 30% mass ratio of Li-NiO from 400 ℃ to 650 ℃. At high temperature, as shown in Fig. 2 (b), the Li-NiO curves are similar with two deformed semicircular arcs at high frequency which partially overlap each other and corresponds to the two electrochemical reactions. For the lower frequencies, the curves of Li-NiO also shows the beginning of another semicircular arc which might correspond to the reaction of a metallic wire of the electrode with the melt. With the decrease of the temperature, the diameters of Li-NiO arcs largely increase, implying that the reaction time is increasing. It also shown in Fig. 2 (a) that the Li-NiO curves at 400 ℃ and 450 ℃ are severely deformed and composed of several arcs. That's because that the eutectic salt has not reached its melting point and all the electrochemical reactions are very slow.

Fig. 3 presents the Nyquist diagram of the composite cathode with different mass ratio of Li-NiO at 650 ℃. The diameters of the deformed semicircular arcs increase with decrease of Li-NiO mass ratio, implying the oxygen reduction reaction is the right time limiting reaction. Fig. 4 shows the interface resistance of the cathode/electrolyte, which decrease with the increase of temperature and mass ratio of Li-NiO.

4 CONCLUSION

The new Li-NiO cathode materials possess only NiO crystal structure. At high temperature, the Li-NiO curves are similar with two deformed semicircular arcs at high frequency which partially overlaps each other and corresponds to two electroche-

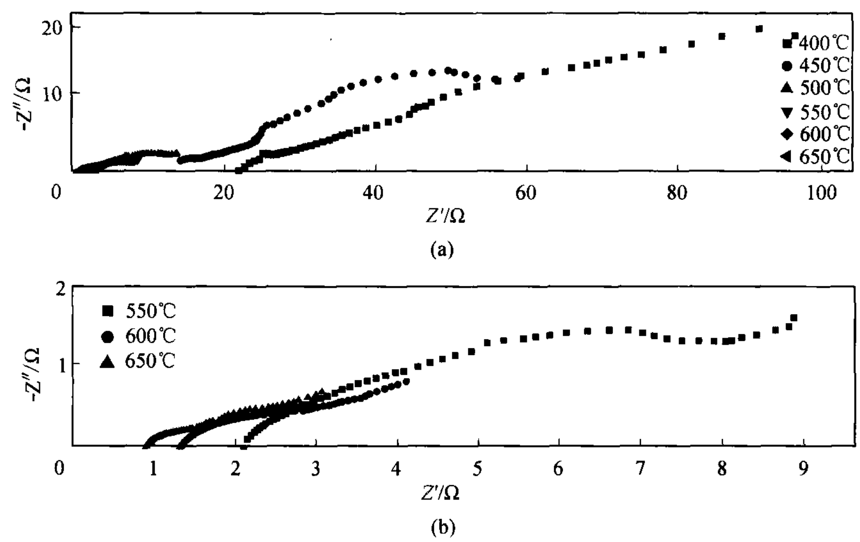

Fig. 2 Nyquist impedance spectrum for Li-NiO/CSLK composite cathode from 400 ℃ to 650 ℃ with the Li-NiO mass ratio of 30%

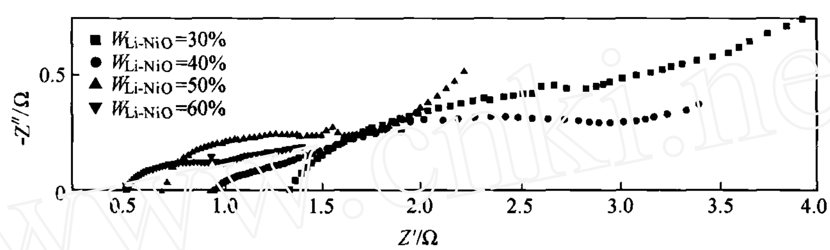

Fig. 3 Nyquist impedance spectrum of Li-NiO/CSLK composite cathode with different mass ratio of Li-NiO at 650 ℃

emical reactions. The diameters of the deformed semicircular arcs increase with the decrease of Li-NiO mass ratio due to the increase of active area for oxygen reduction reaction. The interfacial resistances of cathode/electrolyte decrease with the increase of temperature and the mass ratio of Li-NiO due to the change of microstructure and the decrease of active area of the composite cathode.

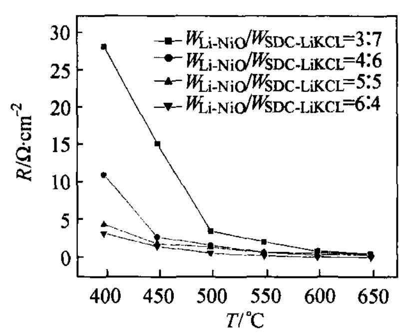

Fig. 4 Interfacial resistance of Li-NiO-CSLK/CSLK at 400—650 ℃ with different mass ratio of Li-NiO

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