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An intermediate temperature fuel cell based on composite electrolyte of carbonate and doped barium cerate with $\text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta}$ cathode

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ABSTRACT

BaCeO$_3$-based proton conductor $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ (BCZYZn) was adopted as a part of the oxide-carbonate composite electrolyte. The total ionic conductivity of BCZYZn-carbonate composite is 0.28 S cm$^{-1}$ at 500 °C. Perovskite oxide $\text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta}$ was developed and used as cathode. It was found that $\text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta}$ exhibits a primitive cubic structure with space group Pm$ar{3}$m(221); $a = 3.8790(1)$ Å, $V = 58.364(1)$ Å$^3$. The electrical conductivity of $\text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta}$ is 15 - 26 S cm$^{-1}$ in the temperature range 400-700 °C measured by d.c. method. Single cell with BCZYZn-carbonate composite electrolyte and $\text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta}$ cathode was fabricated and tested with humidified $\text{H}_2$ (~3 vol% $\text{H}_2\text{O}$) as fuel and air as oxidant. A similar configuration cell with lithiated NiO cathode was also constructed for comparison. It was found that neither $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ nor $\text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta}$ is chemically compatible with $(\text{Li,Na})_2\text{CO}_3$. The fuel cell performance is not as good as those based on doped ceria-carbonate electrolytes.

Keywords: oxide-carbonate composite, conductivity, perovskite, cathode, fuel cell.

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1. Introduction

The current research trend for solid oxide fuel cells is to bring down the working temperature from 800-1000 °C to 400-600 °C, in order to reduce the fabrication cost and improve the durability. Recently, doped-ceria and carbonate composite materials have drawn increasing attentions for their exceptional high conductivity at temperature 400-600 °C \([1-10]\). The composite normally employ doped-ceria oxide as substrate matrix to allow the carbonates distributed inside. Ionic conductivity of \(\sim 0.1\) S cm\(^{-1}\) can be reached at temperature close to the melting point of carbonates \([3]\) and excellent cell performance with maximum power density of \(\sim 1\) W cm\(^{-2}\) has been achieved \([11]\). Besides \(\text{O}^2-\) conducting doped ceria, \(\text{LiAlO}_2\) was also mixed with \((\text{Li/Na})_2\text{CO}_3\) to form a composite electrolyte and a maximum output power density of 466 mW cm\(^{-2}\) has been achieved at 650 °C \([12]\).

Proton-conducting oxides such as doped barium cerates have been widely studied as electrolytes for SOFCs \([13-17]\). This perovskite-type oxide shows mixed proton and oxide-ion conductivity \([16]\) at intermediate temperature in humid atmospheres and its proton conductivity can be significantly enhanced by various rare earth ions doping \([18-22]\). Unfortunately, most doped barium cerates are not stable in the presence of \(\text{CO}_2\) and the stability has been improved when some cerium ions at B-sites were replaced by zirconium ions \([20,23]\). Zhu and Schober et al. reported to mix proton conductor \(\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}\) or \(\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}\) with carbonates to form composite materials \([24,25]\). Huang et al. reported the conductivity of \(\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}\) - \((\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3\) composite electrolyte and a power density of 114 mW/cm\(^2\) has been achieved for a \(\text{H}_2/\text{air}\) fuel cell based on this composite electrolyte \([26]\). In these proton conducting oxides, \(\text{BaCe}_{0.5}\text{Zr}_{0.5}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}\) (BCZYZn) exhibits conductivity over 10 mS cm\(^{-1}\) above 600 °C in wet 5% \(\text{H}_2\) \([20]\). This oxide is also stable in pure \(\text{CO}_2\) at high temperatures. Introduction of a small amount of zinc at B-site can significantly reduce the sintering temperature of \(\text{BaZrO}_3\)-based oxides. To the best of our
knowledge, there is no report on using stable proton-conducting oxide BCZYZn as a part of an oxide-carbonate composite electrolyte. Apart from the electrolyte, the cell performance is greatly affected by the property of cathode. In our previous study, we demonstrated that traditional lithiated NiO cathode used for molten carbonate fuel cells (MCFCs) suffer the same problem when being used for ceria-carbonate composite fuel cell [7]. Lithiation NiO could gradually diffuse into the composite electrolyte and cause performance degradation. Therefore, it is well worth to explore new cathode material for this kind of composite electrolyte. It has been demonstrated that stable fuel cell performance has been achieved when perovskite oxide \( \text{Sm}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta} \) was used as cathode for fuel cells based on oxide-carbonate composite electrolyte[27]. In this work, a new perovskite oxide \( \text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta} \) was also synthesized and used as the cathode in a fuel cell based on BCZYZn-carbonate composite electrolyte. For comparison, single cells were fabricated by one-step co-pressing-sintering process with \( \text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta} \) and lithiated NiO as cathode respectively. Humidified \( \text{H}_2 (~3 \text{ vol\% H}_2\text{O}) \) was used as fuel and air as oxidant at the cathode.

2. Experimental

\( \text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta} \) (BCZYZn) was synthesized by solid state reaction combined with impregnation method. Stoichiometric quantities of \( \text{BaCO}_3, \text{CeO}_2, \text{ZrO}_2 \) and \( \text{Y}_2\text{O}_3 \) were ball-milled for 2 hours in 2-propanol and subsequently dried at 50 °C for 24 hours. The powders were calcined at 1200 °C for 2 hours and then ball-milled again for 2 hours and dried. Zn was introduced by impregnation method. Calculated amount of \( \text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O} \) was dissolved in deionized water and the obtained dried powders were added to the solution under stirring. The slurry was dried at 80 °C in air for 24 hours and fired at 1300 °C for 5 hours to obtain single phase BCZYZn. The composite electrolyte was made by mixing the BCZYZn powders and carbonate salts (53/47 mol%, \( \text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3 \)) at weight ratio of 60/40 then fired at 700 °C for 1 hour before subsequently being quenched in air.
SrFe_{0.7}Mn_{0.2}Mo_{0.1}O_{3-δ} (SFMMo) cathode was prepared by glycine-nitrate combustion process. Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$·9H$_2$O, (CH$_3$CO$_2$)$_2$Mn·4H$_2$O and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were used as metal precursors and dissolved in deionized water. The solution was heated under continually stirring and glycine (NH$_2$CH$_2$COOH) was added at a glycine/metal molar ratio of 2:1. The solution was further heated until spontaneous ignition occurred. The as-prepared powders were subsequently calcined at 1000 °C for 3 hours to obtain single phase SFMMo. The powders were pressed into pellets with a diameter of ~ 13mm and thickness ~ 2mm then fired at 1300 °C for 4 hours. Silver electrode was coated on both sides of the fired pellets for conductivity measurement. Lithiated NiO with composition Li$_{0.3}$Ni$_{0.7}$O was synthesized by the same method as described elsewhere [28].

X-ray diffraction (XRD) data were conducted at room temperature using a Panalytical X'Pert Pro diffractometer with Ni-filtered CuKα radiation using 40 kV and 40 mA (λ = 1.5405 Å), fitted with a X'Celerator detector. Absolute scans were recorded in the 2θ range 5-100° with a step size of 0.0167°.

For conductivity measurement, the as-prepared composite electrolyte was pressed into pellets with diameter of ~ 13mm and thickness of ~ 2mm, then fired at 600 °C for 30 minute. After coated a layer of silver paste on both sides, the conductivity was measured by a.c. impedance method. AC impedance spectroscopy and fuel cell performances were tested by a Solartron 1250 Frequency Response Analyser coupled to a 1287A Electrochemical Interface using CorrWare/CorrView software. Electrical conductivity of SFMMo was measured by a pseudo-four-probe d.c. method using a Solartron 1470 at constant current mode.

Single cell was fabricated by dry-pressing anode (NiO/electrolyte at 50/50wt%), electrolyte and cathode (electrolyte/SFMMo at 50/50wt% with starch) at simple one-step under 300MPa. The cell was sintered at 550 °C for 1 hour with an effective
working area of 0.5 cm$^2$. The thickness of anode, electrolyte and cathode was 0.3 mm, 1 mm and 0.2 mm, respectively and this was carefully controlled by weighing the amounts of powders added. Silver paste was used on each side of the electrodes to improve electrical contact. As silver itself is a good cathode for intermediate temperature fuel cells, it cannot be ruled out that the fuel cell performance could be improved due to the use of silver as current collector. Wet hydrogen (~3 vol% H$_2$O) with a flow rate of 100 ml min$^{-1}$ was supplied as fuel while the cathode side was open to air. The fuel cell measurement set-up has been reported elsewhere [7].

3. Results and discussion

Fig. 1a shows the XRD patterns of BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ (BCZYZn) and BCZYZn-carbonate composite. BCZYZn expresses single phase with cubic structure. The lattice parameter was calculated at $a = 4.3273$ (1) Å. The conductivity of pure BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ and BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$-(Li,Na)$_2$CO$_3$ composite is shown in Fig. 2. The conductivity of pure BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ gradually increased at higher temperatures and reached 0.01 S cm$^{-1}$ at 700 °C. For the composite, the conductivity is in the range of $10^{-6}$ S cm$^{-1}$ at 300 °C but reached 0.28 S cm$^{-1}$ at 500 °C. At 400 °C, the total conductivity of the composite is comparable to pure BCZYZn but the composite exhibits much higher conductivity at a temperature above 400 °C which could be related to the defects at the oxide/carbonate interface [29,30]. On the other hand, when the temperature approaches the melting point, the carbonates become ‘soft’. Therefore the mobility of various ions (Na$^+$, Li$^+$, H$^+$, and CO$_3^{2-}$) was significantly increased, leading to high ionic conductivity. This phenomenon of sharp increase of conductivity has been observed in our precious study of ceria-carbonate composites [6,7]; however, the conductivity of BCZYZn-carbonate composite is slightly higher compared to Ce$_{0.8}$Gd$_{0.05}$Y$_{0.15}$O$_{1.9}$ (GYDC) carbonate composite (0.18 S cm$^{-1}$ at 500 °C) [6].

Single phase of SrFe$_{0.7}$Mn$_{0.3}$Mo$_{0.1}$O$_{3-\delta}$ was obtained when the sample was fired at 1100 °C. To obtain high quality refinement, XRD pattern from well-crystallized sample fired at 1300 °C was used for Rietveld refinement using software GSAS [31].
It was found that SrFe$_{0.7}$Mn$_{0.3}$Mo$_{0.1}$O$_{3-\delta}$ exhibit a primitive cubic structure with space group $P m\bar{3}m(221)$; $a = 3.8790(1)\,\text{Å}$, $V = 58.364(1)\,\text{Å}^3$. This is the same structure as reduced SrMn$_{0.5}$Nb$_{0.5}$O$_{2.875}$ [32]. In this structure, Fe, Mn and Mo ions are randomly distributed at the B-site. The refinement also indicates that the occupancy of oxygen is 0.97 which means that the obtained SrFe$_{0.7}$Mn$_{0.3}$Mo$_{0.1}$O$_{3-\delta}$ is an oxygen deficient oxide. It should also be noted that XRD is not sensitive to light atom such as oxygen. Neutron diffraction is necessary for more accurate determination. The XRD pattern of SrFe$_{0.7}$Mn$_{0.3}$Mo$_{0.1}$O$_{3-\delta}$ is shown in Fig. 3 and refined lattice parameters are listed in Table 1.

Fig. 4 shows the d.c. conductivity of SrFe$_{0.7}$Mn$_{0.3}$Mo$_{0.1}$O$_{3-\delta}$ between 40 and 700 °C. The total conductivity was 15–26 S cm$^{-1}$ between 400–700 °C which is adequate to be used as cathode materials for fuel cells.

Single cells with SFMMo cathode were fabricated by co-pressing the tri-layer of anode, electrolyte and cathode at single step and fired at 550 °C for 1 hour. The cell performance was evaluated using H$_2$ as fuel, air as oxidant. The results are shown in Fig. 5a. Open circuit voltages (OCVs) of 1.06, 1.02 and 1.01 V were obtained at temperatures 500, 525 and 550 °C respectively. These OCVs are very close to the theoretical value and comparable to the result of fuel cells based on ceria-carbonate composite [6, 7], indicating that the electrolyte was gas tight. The maximum power densities were 62, 102 and 160 mW cm$^{-2}$ at 500, 525, and 550 °C, respectively. These performances are comparable to the results of other pervoskite oxides such as La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) and La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) used as cathode for the ceria-carbonate composite based fuel cells [33]. The performance is lower than those with ceria-carbonate composite as electrolytes. The impedance spectra of the cell under open circuit conditions were measured at temperature 500-550 °C as shown in Fig. 5b. The series resistances $R_s$ (intercept with real axis at high frequency) are 0.71, 0.56 and 0.36 Ωcm$^2$ at 500, 525 and 550 °C respectively. The total resistances $R_t$ (intercept with real axis at low frequency) are 3.48, 3.29 and 3.05 Ωcm$^2$ at 500, 525
and 550 °C respectively. Therefore, the electrode polarization resistances (Rp) of the cell are considered as the difference between Rf and Rs, which are 2.77, 2.73 and 2.69 Ω cm² at 500, 525 and 550 °C. Slightly higher polarization resistance was observed at 525 °C which might be related to microstructure change at the electrodes due to the melting and/or diffusion of molten carbonate components. Further investigation is required. Clearly, the major polarization resistance is from the electrode and/or electrode-electrolyte interface.

For comparison, a similar configuration single cell was also fabricated with Li0.3Ni0.7Oy cathode and cell performance is shown in Fig. 6a. OCVs of 1.09, 1.03 and 1.01 V were observed at 500, 525 and 550 °C respectively. The maximum power density at 550 °C is 183 mW cm⁻² which is slightly higher than that for the cell with SFMMo cathode. Various polarization resistances are showed in Fig. 6b. Series resistance Rs were 0.23, 0.17 and 0.15 Ω cm² while the corresponding Rp were 1.69, 1.21 and 0.87 Ω cm² at 500, 525 and 550 °C respectively. The resistances are comparable to the values when GYDC was used as part of the oxide-carbonate composite [7], due to the high conductivity of BCZYZn-carbonate composite at lower temperature. The large electrode polarization could be related to the microstructure and composition of electrodes and further optimization is required.

After the fuel cell test, some reactions between BCZYZn and carbonates were observed as shown in Fig. 1b. BaCO₃, Ba(CeₓZr₁₋ₓ)O₃ and CeO₂ were formed in the composite. As BCZYZn is stable in pure CO₂, for formation of BaCO₃ is believed due to the reaction between BCZYZn and carbonate with the leaching of CeO₂. The formed BaCO₃ may affect the catalytic activity of electrode leading to higher polarization resistance and lower fuel cell performance. The ionic conductivity of the BaCZYZn-carbonate was not affected as the series resistance is about 0.2 Ω cm² around 525 °C.

In order to further identify the reason for the different fuel cell performance when SrFe₀.₇Mn₀.₃Mo₀.₁O₃₋δ and Li₀.₃Ni₀.₇Oy was used as the cathode respectively, the
chemical compatibility between the electrolyte and SFMMO cathode was carried out by XRD study. As the different components in the composite electrolyte, BCZYZn and (Li,Na)\textsubscript{2}CO\textsubscript{3} react with each other (Fig. 1b), SFMMO was mixed with BCZYZn or (Li,Na)\textsubscript{2}CO\textsubscript{3} separately with a weight ratio of 50/50. After firing the SFMMO/BCZYZn mixture at 600 °C for 10 hours, it was found that the two oxides are compatible with each other (Fig. 7b). However, after firing the SFMMO/(Li,Na)\textsubscript{2}CO\textsubscript{3} mixture at the same condition, the room temperature XRD pattern indicates that the main phase is SrCO\textsubscript{3} (PDF Card No. 01-074-1491) (Fig. 7c). There are two unidentified peaks. This experiment indicates that SFMMO is not chemically compatible with the mixed carbonate. In SFMMO, A-sites are only occupied by alkaline earth element strontium rather than doped with rare earth elements such as Sm, La etc., therefore the activity of strontium is very high thus easy to react with carbonates to form stable SrCO\textsubscript{3}. Partial replacement of Sr by rare earth element may make this perovskite oxide compatible with carbonates. Diffraction peaks for oxides containing Fe, Mn, Mo were not observed, possibly in amorphous state. The reaction between SFMMO cathode and mixed carbonate may cause the lower fuel cell performance comparing to that with Li\textsubscript{0.3}Ni\textsubscript{0.7}O\textsubscript{y} cathode.

4. Conclusion

BaCeO\textsubscript{3}-based proton conductor BaCe\textsubscript{0.5}Zr\textsubscript{0.3}Y\textsubscript{0.16}Zn\textsubscript{0.04}O\textsubscript{3-}\textsubscript{δ} (BCZYZn) was employed as part of the oxide-carbonate composite electrolyte. New perovskite oxide SrFe\textsubscript{0.7}Mn\textsubscript{0.2}Mo\textsubscript{0.1}O\textsubscript{3-}\textsubscript{δ} (SFMMo) was synthesized and used as cathode for the composite fuel cell. It was found that SrFe\textsubscript{0.7}Mn\textsubscript{0.2}Mo\textsubscript{0.1}O\textsubscript{3-}\textsubscript{δ} exhibits a primitive cubic structure with space group Pm\textsubscript{3}m(221); a = 3.8790(1) Å, V = 58.364(1) Å\textsuperscript{3}. The electrical conductivity of SFMMo is 15–26 S cm\textsuperscript{-1} in the temperature range 400–700 °C. Single cells with SFMMo and lithiated NiO cathodes were tested and compared. It was found that BCZYZn and carbonate react with each to form BaCO\textsubscript{3} and new oxides during the fuel cell measurements. The chemical compatibility between BaZr\textsubscript{0.8}Y\textsubscript{0.2}O\textsubscript{3-δ} and (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3} is good but the fuel cell performance is not ideal\cite{26}. The fuel cell performance based on either BCZYZn-carbonate or
BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ - (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ composite electrolyte is not as good as those based on doped ceria-carbonate composite electrolytes. The chemical reaction between BCZYZn and (Li,Na)$_2$CO$_3$ in the electrolyte indicates BCZYZn-(Li,Na)$_2$CO$_3$ composite is not a good electrolyte for intermediate temperature fuel cells. So far composite electrolytes based on doped ceria are still the best choice.

Acknowledgements

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Captions

Table 1 Structure parameters of SrFe$_{0.7}$Mn$_{0.2}$Mo$_{0.1}$O$_{3-\delta}$.

Fig. 1 XRD of pattern of BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ (BCZYZn) (a) and BCZYZn-carbonate composite after fuel cell test (b).

Fig. 2 Temperature dependence of conductivity of BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ - (Li,Na)$_2$CO$_3$ composite in air.

Fig. 3 XRD pattern of SrFe$_{0.7}$Mn$_{0.2}$Mo$_{0.1}$O$_{3-\delta}$. Data were collected at room temperature from a sample fired at 1300 °C for 4 hours.

Fig. 4 Temperature dependence of conductivity of SrFe$_{0.7}$Mn$_{0.2}$Mo$_{0.1}$O$_{3-\delta}$ in air.

Fig. 5 The performance of single cell with SrFe$_{0.7}$Mn$_{0.2}$Mo$_{0.1}$O$_{3-\delta}$ cathode (a) dependence of cell voltages and power densities on current densities and (b) corresponding impedances.

Fig. 6 The performance of single cell with lithiated NiO cathode (a) dependence of cell voltages and power densities on current densities and (b) corresponding impedances.

Figure 7 The XRD pattern of the SFMMO cathode (a), the SFMMO and BCZYZn mixture after firing at 600 °C (b), the SFMMO and (Li,Na)$_2$CO$_3$ mixture after firing at 600 °C (c).
Table 1 Structure parameters of SrFe$_{0.7}$Mn$_{0.2}$Mo$_{0.1}$O$_{3.5}$.

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Note: Space group Pm$\bar{3}$m(221); $a = 3.8790(1)\text{Å}$, $V = 58.364(1)\text{Å}^3$. $R_{wp} = 9.21\%$, $R_p = 6.38\%$, $\chi^2_{red} = 3.212$. 
Fig. 1 XRD of pattern of BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ (BCZYZn) (a) and BCZYZn-carbonate composite after fuel cell test (b).
Fig. 2 Temperature dependence of conductivity of pure BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ and BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$–(Li,Na)$_2$CO$_3$ composite in air.
Fig. 3 XRD pattern of SrFe$_{0.7}$Mn$_{0.2}$Mo$_{0.1}$O$_{3-δ}$. Data were collected at room temperature from a sample fired at 1300 °C for 4 hours.
Fig. 4 Temperature dependence of conductivity of SrFe0.7Mn0.2Mo0.1O3-δ in air.
Fig. 5 The performance of single cell with \( \text{SrFe}_{0.7}\text{Mn}_{0.2}\text{Mo}_{0.1}\text{O}_{3-\delta} \) cathode (a) dependence of cell voltages and power densities on current densities and (b) corresponding impedances.
Fig. 6 The performance of single cell with lithiated NiO cathode (a) dependence of cell voltages and power densities on current densities and (b) corresponding impedances.
Figure 7 The XRD pattern of the SFMMO cathode (a), the SFMMO and BCZYZn mixture after firing at 600 °C (b), the SFMMO and (Li,Na)$_2$CO$_3$ mixture after firing at 600 °C (c).