Short communication

Single-component and three-component fuel cells

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ABSTRACT

Single-component and three-component fuel cell devices have been studied using mixed ionic and electronic conductor. The three-component fuel cell means a conventional fuel cell which is the configuration consists of anode, electrolyte and cathode; while the single-component fuel cell uses only one component that can function as the electrodes and electrolyte simultaneously. The single-component fuel cell showed the same or even better performance compared to conventional three-component fuel cell. A maximum power density of $700\,mW\,cm^{-2}$ has been achieved by the single-component fuel cell at $550\,°C$.

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1. Introduction

Recently we have developed a single-component fuel cell (FC) using only one component which can function as the electrodes and electrolyte simultaneously [1]. In this work, a significant improvement of this novelty device performance is achieved by developing new functional nanocomposite materials. These works are based on innovative solid oxide fuel cells working in intermediate and low temperature ($300–700\,°C$) [2–5], especially, the new fuel cell research strategy of NANOCOFC (Nanocomposites for advanced fuel cell technology) [6] explored and developed for low temperature solid oxide fuel cells (LTSOFCs) [7–13]. This nanocomposite approach was designed and fabricated by utilizing the two-phase interfaces as express paths for ionic conduction as well as functions for compatible nanocomposite electrodes [14,15]. In previous studies, some metal oxides, e.g. $LiNiO_2$, $LiNiCuO_x$, $LaNi_{0.2}Fe_{0.65}Cu_{0.15}O_3$ $LiNiZnFeO_x$ etc., exhibited good catalytic activity as both anode and cathode materials. Symmetrical configuration of LTSOFCs devices with these metal oxides electrode have achieved excellent performances combined with the ceria-composite electrolytes [16]. These innovative researches and developments make it possible to use a single component to realize the fuel cell function. The single-component is only one homogenous mixture layer with the ionic and electronic conducting materials. In this work, we further report a new functional composite material possessing both electronic and ionic conductivities with significant improvement

of the single-component device performances from $450\,mW\,cm^{-2}$ to $700\,mW\,cm^{-2}$ at $550\,°C$. The studies were also carried out compared with conventional three-component fuel cells.

2. Experimental

The material for single-component FC was prepared based on two types of materials: one was the ionic conductor and the other one was electronic conductor. In this work, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC)–Na_2CO_3 (NSDC) nanocomposite was used as ionic conductor and the LiNiCuZnFe-composite metal oxides was used as electronic conductor.

The NSDC was prepared by one-step co-precipitation process [16]. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ (99%, Sigma–Aldrich, USA) and $Sm(NO_3)_3 \cdot 6H_2O$ (99.9%, Sigma–Aldrich, USA) were mixed and dissolved in de-ionic water to form a 0.5 M solution. The solution was stirred at $80\,°C$ for 0.5 h. Then Na_2CO_3 (99.0%, Sigma–Aldrich, USA) solution (0.5 M) used as a precipitation agent, was added into the solution with a molar ratio of $(Ce^{3+} + Sm^{3+})$: CO_3^{2-} = 1:2 under vigorous stirring to form a white precipitation. The precipitate was then filtrated and dried in an oven at $120\,°C$ for 8–10 h. Finally, the NSDC precursor was sintered in a furnace at $800\,°C$ for 4 h. The resulting material was ground completely to obtain homogenous NSDC nanocomposite powders.

In parallel, a mixed solution of LiOH (≥98%, Sigma–Aldrich, USA), $Ni(NO_3)_2 \cdot 6H_2O$ (≥98.5%, Sigma–Aldrich, USA), $Cu(NO_3)_2 \cdot 3H_2O$ (99–104%, Sigma–Aldrich, USA), $Zn(NO_3)_2 \cdot 6H_2O$ (98%, Sigma–Aldrich, USA), and $Fe(NO_3)_3 \cdot 9H_2O$ (99.0%, Merck, Germany) were prepared in a molar ratio of Li:Ni:Cu:Zn:Fe = 0.15:0.25:0.1:0.2:0.3. Then appropriate amount of

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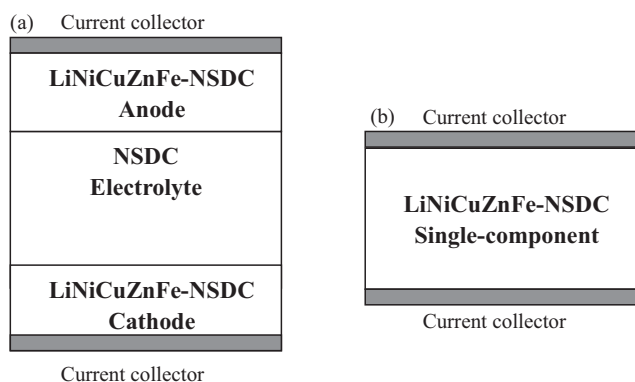E-mail address: binzhu@kth.se (B. Zhu).

Fig. 1. Schematics for constructions of conventional three-component fuel cell device (a) and single-component fuel cell (b).

Fig. 2. (a) XRD pattern of as-prepared LiNiCuZnFeO$_x$–NSDC composite material and (b) SEM picture of as-prepared LiNiCuZnFeO$_x$–NSDC composite material.

the NSDC powder was added into the LiNiCuZnFe-nitrate solution. The mixture suspension was stirred and dried at 80 °C in air. Then the precursor was calcined at 700 °C in air for 2 h and cooled to room temperature to form LiNiCuZnFeO$_x$–NSDC composites.

The crystal structure of as-prepared composite material was identified by X-ray powder diffraction (XRD) with a Philips X'pert pro super diffractometer using Cu Kα radiation (λ = 1.5418 Å). The microstructure of sample was investigated by a Zeiss Ultra 55 field emission scanning electron microscopy (FESEM).

Two types of fuel cell devices were fabricated. Type I: conventional three-component device made of anode, electrolyte and cathode; Type II: single-component device using only on layer of LiNiCuZnFeO$_x$–NSDC mixture. The schematic diagram of these two types of cells was shown in Fig. 1. For type I cells, the as-prepared LiNiCuZnFeO$_x$–NSDC sample was used as for both anode and cathode catalysts, and NSDC was used as the electrolyte. The anode, electrolyte and cathode were uniaxially pressed to form a sandwich structure within a die under 250 MPa. The resulting cell size is 13 mm in diameter and 0.1 cm in thickness consisting of 0.05 cm for anode, 0.02 cm for electrolyte and 0.03 cm for cathode, respectively. For type II cell, the LiNiCuZnFeO$_x$–NSDC sample was pressed as tablet with 13 mm in diameter under 250 MPa. Same thickness of 0.1 cm was also maintained. For these cells, silver paste was applied on one surface of pellet and the nickel-foam was used on the other surface as the current collectors. The fuel cell with an active area of 0.64 cm^2 was tested from 450 to 580 °C, where hydrogen and air were used as fuel and oxidant, respectively. The gas flow rates were controlled in the range of 80–120 ml min^{-1} at 1 atm pressure.

3. Results and discussion

The XRD pattern of as-prepared LiNiCuZnFeO$_x$–NSDC material is shown in Fig. 2a. It can be seen that the material is mainly consists of individual oxides. One major phase of the material is SDC. It was attributed that NSDC had only CeO$_2$ diffraction peaks since the NSDC was a core–shell structure with an amorphous Na$_2$CO$_3$ shell [12]. Besides, NiO, LiFeO$_2$, CuO and ZnO can be identified. It is obvious that the synthesized material is a mixture of all these oxides in a composite way between the ionic and electronic metal oxide conductors. It should be noted that metal oxides, e.g. NiO, CuO, ZnO, and LiFeO$_2$ are actually semiconductors. For example, NiO is p-type conductor and the doping with other metal can make its conductivity increases significantly [17,18]. ZnO is a typical electronic conductor [19], when doped with Li$^+$ it can achieve significant p-type conductivity [19,20]. Besides, NSDC is also common to possess of dual H$^+$ and O^{2-} conduction while situated in H$_2$ containing atmosphere, e.g. in a fuel cell environment [21]. Therefore, as prepared LiNiCuZnFeO$_x$–NSDC material can satisfy the basic requirements of
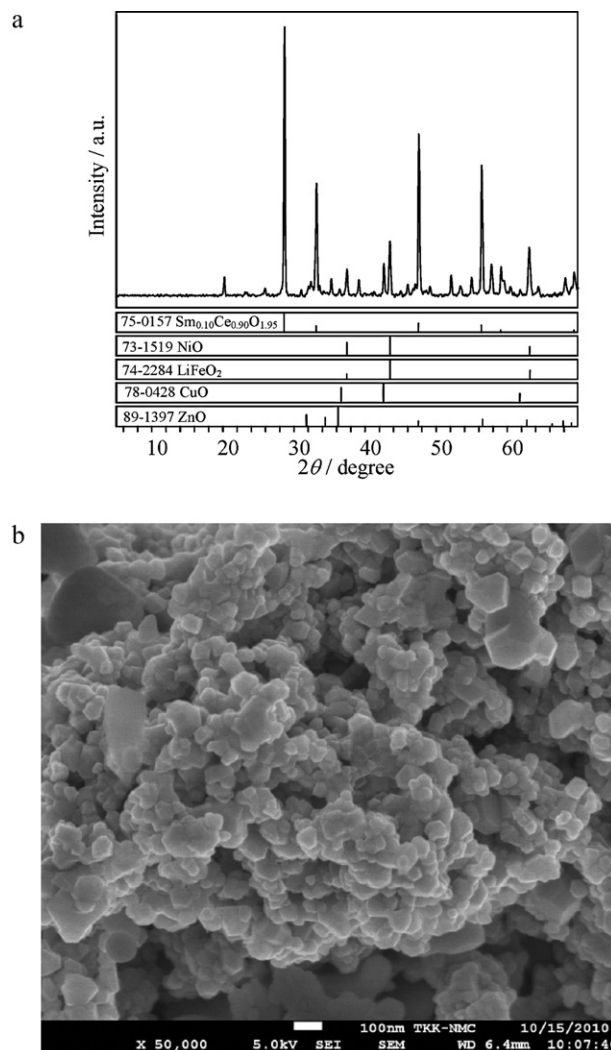
electrode materials for SOFCs and may be used as both anode and cathode materials in the conventional three-component fuel cell devices.

It should be noticed that the prepared LiNiCuZnFeO$_x$–NSDC has the same properties as an electrode material used in conventional three-component fuel cell in which the electrodes, anode and cathode, are always prepared in a mixture of the electronic (catalyst material) and ionic (electrolyte material) conductors in a composite type. Directly one-step preparation of the LiNiCuZnFeO$_x$–NSDC composite with a wet-chemical process may obtain a better homogeneity as shown in Fig. 2b. It can be seen that all particles of the as-prepared sample are distributed in a very homogenous configuration, which might further improve the electrode performance by enlarging the triple phase boundary and taking advantages of Ni, Cu, Fe catalytic activities.

Fig. 3a shows I–V and I–P characteristics for the single-component devices using the LiNiCuZnFeO$_x$–NSDC composite simultaneously as electrodes and electrolyte. In comparison, the performances for conventional three-component fuel cell device are also included. Fig. 3b shows further corresponding I–V and I–P characteristics for the single-component device operated at various temperatures. The three-component fuel cell exhibits a maximum power density of near 700 mW cm^{-2} at 550 °C. It demonstrated that the prepared LiNiCuZnFeO$_x$–NSDC composite can function as
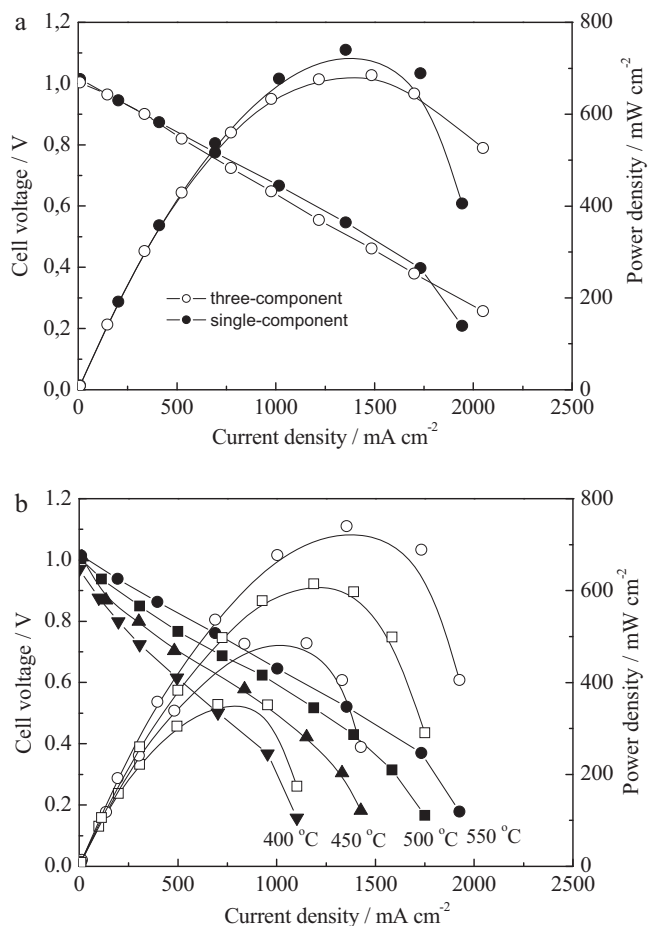
Fig. 3. (a) *I–V* and *I–P* characteristics for the single component fuel cell in comparison to the conventional three-component fuel cell at 550 °C and (b) *I–V* and *I–P* characteristics for the single component fuel cell at various temperatures.

Fig. 4. (a) OCV setup processes against the gas supplier of H_2 and O_2 (air) and (b) devices discharging performances under a constant load, device voltage vs. time.

both anode and the cathode simultaneously. The result indicates that the $LiNiCuZnFeO_x$ has also excellent catalytic activity towards hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). Compared to the conventional three-component fuel cell, even slightly better performance of more than 700 mW cm^{-2} has been achieved by the single-component device at 550 °C. Fig. 4a displays the relationship of open circuit voltage (OCV) against gas suppliers. It can be seen that device OCVs show fast responses from positive ca 1.0 V to negative 1.0 V as soon as exchange H_2 and air supplies. The single-component device exhibits faster response process (less than 15 s) to reverse the OCV set up compared with that of the three-component device (more than 40 s). These results further demonstrate that, (i) the as-prepared $LiNiCuZnFeO_x$–NSDC material exhibits good catalytic activity towards HOR and ORR; and (ii) the single-component device has a faster kinetic process than that of the three-component device. It might be attributed to the removing of two interfaces of anode/electrolyte and electrolyte/cathode in the single component device. In addition, the interfaces between electrolyte and electrodes contributed to major polarization losses, which delayed the kinetic responses [22].

Further studies on the Ag and Ni-foam roles were performed. The results showed that Ag and Ni-foam have some catalytic function to cell voltage, but contribute negligible current outputs to the device. In this case, if both Ag and Ni-foam act for same function as the current collect, then it is reasonable that the showed data as completely symmetric when switching the two electrodes to be either anode or cathode.
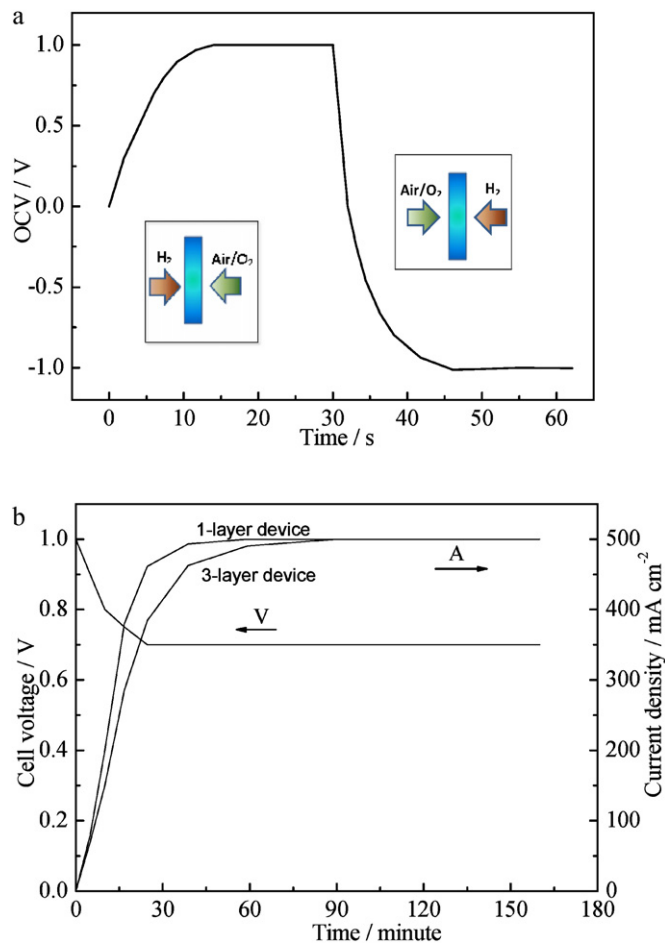
On the other hand, since Fig. 4a shows that the cell responds in an OCV case without loading, the reaction can take place very fast at the surface of the catalyst. For comparison, we further operated the devices under discharging with a constant loading for 2.5 h as shown in Fig. 4b. Both devices exhibit very stable device performances, i.e. constant current outputs. But the single-component device exhibits a much smaller polarization loss and a shorter process to reach the constant discharging plateau.

In this case, the interfaces can be gradually optimized during the discharging with current passing through. Especially while the H^+ conductivity can be introduced during the current passing through the device in FC environment since the extrinsic nature of the H^+ and NSDC electrolyte [23,24]. Thus ionic conductivity increasing with time to reach a certain stable value, polarization loss will be also decreased being along with the ohmic resistance reducing in the same time. As consequence, the current density is improved as the time increase to reach a steady stable plateau, which is very common in our previous three component fuel cells. In addition, the period of such increasing time is mainly affected by the cell fabrication techniques when the same materials used.

It is interesting to note that the single-component device does not display short circuit at all and even achieves better performance compared to the three-component device. Since the single-component device can perform the same function as fuel cell and convert the chemical energy of H_2 to electricity continuously, the following reactions are proposed:at anode,

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

at cathode,

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{2}$$

overall reactions,

$$H_2 + \frac{1}{2}O_2 \rightarrow 2H^+ + O^{2-} \tag{3a}$$

$$2H^+ + O^{2-} \rightarrow H_2O \tag{3b}$$

Eqs. (3a) and (3b) can be further written as:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{4}$$

Compared to conventional solid oxide fuel cells, the following fuel cell reactions:at anode,

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{5}$$

at cathode,

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{6}$$

overall reaction,

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{7}$$

Both types devices show the same overall reactions, but in the single-component device it takes two steps to realize the overall reaction, i.e. Eq. (3a): H_2 and O_2 are catalyzed, respectively at H_2 and O_2 (air) contacting side into corresponding ions, H^+ and O^{2-}, then Eq. (3b) further subjects combination between H^+ and O^{2-} to form the water and to generate electricity in the same time.

During this process, the H_2 contacting side acts as a "functional" anode to release electrons by forming H^+, and the air (O_2) contacting side as a "functional" cathode to receive electrons. The fuel cell reaction is completed immediately as long as H^+ and O^{2-} appear in close proximity anywhere in the material.

There is an essentially different from the conventional fuel cell, where a pure ionic conducting electrolyte and process are key to realize the fuel cell functions; While in the single-component fuel cell, only one component of a mixture of ion and electron (n and p) conducting materials is used. In this case, there is no electrolyte separator, thus no macro-level bulk electrolyte process.

At this stage, detailed mechanisms for the single-component device are not yet clear, but the comparison study shows the same functions and comparable device performances between the conventional three-component and the single-component devices. It has been observed that the porosity plays an important role to determine the performances of single component. We have determined porosity for the single component after pressing with and without heat-treatments. The heat-treatment at 600 °C for 0.5 h was performed. In both cases the resulting components showed close porosity values of $30.94 \pm 0.088\%$ and $29.35 \pm 0.068\%$, respectively. Also the components exhibited good mechanical strength. We have not yet made efforts for careful control of the porosity in the first aim for demonstration of such single-component devices. We are making efforts by adding some organic binders and different sintering temperatures, also making single component devices with porosity gradient to form porous surfaces but dense in the center part. With these efforts we may control the porosity for finally produced single components and optimize the device performances. It request more carefully works to be reported later.

The single-component devices open a radical new fuel cell research field and new science which is very much worthy for continued R&D and will become a new research strategy in fuel cell R&D. More works have to be done to investigate the detailed mechanism and science of the single-component fuel cell.

4. Conclusions

In this study, comparison studies have been made on the electrochemical performances of the function for single-component and three-component fuel cell devices. It is demonstrated that a single-component device without the electrolyte but only the LiNiCuZnFeO$_x$–NSDC single component which can function as the electrodes and electrolyte simultaneously. The single-component device also realizes the fuel cell functions, i.e. conversion of H_2 and O_2 (via H^+ and O^{2-}) to generate electricity without the conventional electrolyte process. There are a number of advantages for the single-component device compared with the conventional three-component device: (i) better catalyst functions for both H_2 and O_2 which can realize good device performance; (ii) faster kinetic processes because of removal of anode/electrolyte and electrolyte/cathode two interfaces; (iii) better device performances, higher power outputs more than 700 mW cm^{-2} achieved at 550 °C; and (iv) faster electrochemical response processes. From the preliminary results, we anticipate that a new fuel cell science and technology will be developed with significant importance for both fundamental and applied research.

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