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A commercial lithium battery LiMn-oxide for fuel cell applications

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ABSTRACT

Hereby we report first a commercial lithium battery LiMn-oxide (LMO) positive electrode material for fuel cell applications. The obtained LMO can be used for both anode and cathode in a three-layer fuel cell, but displays low electro-catalytic activity and power output. Using a nanocomposite approach we have significantly improved the cell performance from tens mW cm^{-2} up to 210 mW cm^{-2}, which is technically useful for low temperature (bellow 600 °C) ceramic fuel cells. We also constructed single-layer fuel cell using the LMO/SDC–metal oxide composite and achieved even better performances than those for conventional anode–electrolyte–cathode three-layer fuel cells.

1. Introduction

Recent developments on solid oxide fuel cells have been carried out extensively on low temperatures operation, bellow 800 °C for using conventional yttrium stabilized zirconia, doped ceria oxide, and 300–600 °C with functional nanocomposite materials, e.g. ceria-based composites, typically, SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$)–M_2CO_3 (M=Li, Na, K) and ceria–metal oxide, such as LiZn-oxide-SDC composite [1]. NANOCOFC (Nanocomposites for advanced fuel cell technology) approach has demonstrated to be a new effective scientific methodology to develop functional nanocomposite materials to meet low temperature, 300–600 °C, operation demands with worldwide R & D upsurge [2]. Based on NANOCOFC R&D, a breakthrough technology: an electrolyte-free fuel cell (EFFC) has been invented [3,4]. This nanocomposite approach is rationally designed to utilize the phase interface as a highway for ionic conduction as well as to realize high catalytic activity. Originated from this strategy, advanced composite ionically conductive materials, e.g., core–shell [5] and nanowire structural [6] ceria-based nanocomposite possessing exceptional ionic conductivity (over 0.1 S cm^{-1} above 300 °C) and unique H^+/O^{2-} simultaneous conduction property [7,8], were developed. The NANOCOFC and EFFC approaches have successfully explored wide material feasibilities for next generation fuel cell technologies. In this work, we report to use and modify the commercially available lithium battery cathode material, LiMn-oxide, through the NANOCOFC approach for fuel cell application, with the aim to demonstrate both its technical feasibility and commercial potentials.

2. Experimental

Both LiZnO-$Sm_{0.2}Ce_{0.8}O_{1.9}$ (LZSDC) and SDC were prepared by one-step co-precipitation method. For LZSDC, stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ (Ce:Sm=0.8:0.2 M ratio) were mixed and dissolved in deionized water to form a 0.5 M solution. $LiOH/Zn(NO_3)_2 \cdot 6H_2O$ (Li:Zn=1:1) 0.5 M solution was made in parallel. Then these two solutions were mixed in volume ratio of 2:1, with stirring and heating at 80 °C. Sodium carbonate solution (0.5 M) as precipitant was added into the above solution with a molar ratio, cation ions:CO_3=1:1.5. The precipitate was filtrated and washed four times with deionized water, followed by alcohol washing, and dried in an oven at 150 °C for 24 h to get the dried precursor, which was then sintered at 750 °C for 2 h in air.

Commercial LiMn-oxide (LMO) was provided by a lithium battery industry (Duo Fu Duo Group, Advanced battery Ltd, Henan, China). The appropriate amount of the as-synthesized LZSDC was mixed with LMO in various weight ratios and ground completely. The mixture was also ground thoroughly in alcohol to enhance the interfacial contacts.

Powder X-ray diffraction (XRD) patterns of as-prepared samples were recorded on a D8 Advance/PC X-ray diffractometer (Germany, Bruker Corporation), using Cu *K*a as the source.

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The morphologies of the samples were examined in a JSM7100F field emission scanning electron microscope (FESEM, Japan).

Fuel cells were constructed in two configurations: anode/electrolyte/cathode three-layer and single-layer configuration. In the three-layer device (TLD), the LZSDC was the electrolyte and LMO/LZSDC were used for both anode and cathode; while the latter was directly used in the single-layer device (SLD).

The details for preparation of a TLD can be found elsewhere [5]. For the SLD, the mixture of the LMO and LZSDC materials were simply pressed as one layer at the same pressure with the same diameter (13 mm) and thickness (1 mm) as the TLDs. Silver paste was coated on one surface of the green tablet and the other using nickel-foam as the current collector. The TLDs and SLDs were provided by H_2 and air at its respective side for fuel cell operation. The fuel cells were measured at 550 °C with flowing hydrogen as fuel (l80–150 ml min^{-1}) and air as the oxidant (150–300 ml min^{-1}). The *I–V* curves of the cells were recorded using a programmable electronic load (IT8811, ITECH, Nanjing).

3. Results and discussion

Fig. 1 displays XRD pattern of the commercial LMO. It is indexed to $Li_{1.6}Mn_{1.6}O_4$ (PDF card No. 52-1841) with good crystalline. Same to the sample prepared by two-step co-precipitation [9], the prepared LZSDC using one-step synthesis shows the same phase structure: LMO and LZSDC composite phases; On the other hand, the sample treated using alcohol grinding, shows weak diffraction reflections, indicating some disorder in crystalline or amorphous structure.

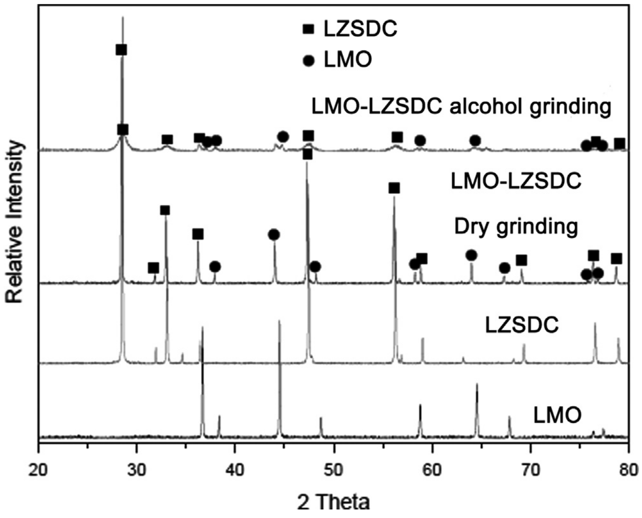

Fig. 1. Room temperature XRD patterns of the commercial LMO and as-prepared samples.

The commercial LMO consists of sub-micrometer particles with crystalline faces orientation (Fig. 2a), while the LZSDC was composed by well dispersed spherical particles (Fig. 2b). The two phases are homogeneously distributed with loose contacts in the mechanically mixed sample (Fig. 2c). A significant change of the particle morphology has been observed in the alcohol grinding sample. The particles were homogenously merged with each other. This is expected to create more interfaces and close contacts for ionic transport and tripe phase boundaries, and promote the fuel cell reactions.

Fig. 3a presents *I–V* characteristics of SLDs using commercial LMO mixed directly with the LZSDC ionic conductor in various compositions. Most compositions show the device OCVs higher than 1.0V which has demonstrated both anodic and cathodic functions of the LMO. The SLD with 40 wt% of LMO presents the highest performance. Such a composite is then subjected to alcohol grinding. The electrochemical performance of the SLD and TLD are also investigated and compared. It can be noticed that the SLD exhibited slightly higher performances than that of the TLD as shown in Fig. 3b.

The above device in the SLD configuration displays the fuel cell reactions as proposed before [10]:

At H_2 contacting side: $H_2 \rightarrow 2H^+ + 2e^-$
At air (O_2) side: $0.5O_2 \rightarrow 2e^- + O^{2-}$
Overall reactions: $H_2 + 0.5O_2 \rightarrow 2H^+ + O^{2-}$

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

Combining the above equations, $H_2 + 0.5O_2 \rightarrow H_2O$

It can be seen clearly from Fig. 3 that in an intermediate composition between the LMO and LZSDC the device displays an optimal performance. Compared with the SLDs with the pure LZSDC and pure LMO, the SLD with LZSDC: LMO = 3: 2 gives a short circuit current density of 360 mA cm^{-2}, one order of magnitude higher than the pure LZSDC case. This is an indication that there is a synergy effect between the ions (LZSDC) and electrons (LMO) in the two-phase composition, which is ascribed to an interfacial mechanism to cause a high ionic transport between two constituent phases. By forming two-phase composites through interaction between

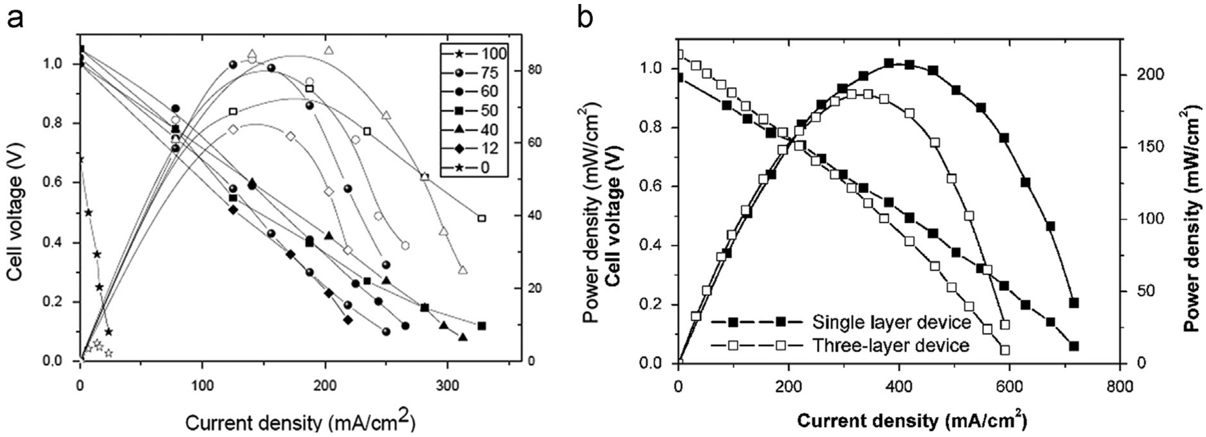

Fig. 3. *I–V* and *I–P* characteristics of fuel cells at 550 °C (a) with unmodified LMO at different compositions, and (b) comparison between SLD and TLD with modified LMO at a composition of LMO:LNCZO = 2:3.