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# Electrochemical study of lithiated transition metal oxide composite as symmetrical electrode for low temperature ceramic fuel cells

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## ABSTRACT

In this work, Lithiated NiCuZnO<sub>x</sub> (LNCZO) composite is synthesized and evaluated as a potential symmetrical electrode for ceria-carbonate composite electrolyte based low temperature ceramic fuel cells. Its crystal structures, the hydrogen oxidation/oxygen reduction electrochemical activities and fuel cell performances are systematically examined on the symmetrical cell configuration. Nano crystallite particles in the form of composite are observed for these oxides. The LNCZO shows relatively high catalytic activities for hydrogen oxidation and oxygen reduction reaction according to the electrochemical impedance spectroscopy measurements. A remarkable low oxygen reduction activation energy of 42 kJ mol<sup>-1</sup> is obtained on the LNCZO/ceria-carbonate composite, demonstrating excellent electro-catalytic activity. Especially, the catalytic activity can be further improved in the presence of water in the cathode chamber. The results show that the lithiated transition metal oxide composite is a promising symmetrical electrode for ceria-carbonate electrolyte and composite approach might a probable solution to develop super-performance electrodes for reduced temperature ceramic fuel cells.

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## 1. Introduction

Fuel cells that operate at low temperatures between 300 and 600 °C are of particular interest, since this temperature range allows for the use of less precious cell components and hydrocarbon fuel, and facilitates simpler cell/stack/module

assembly and operational durability [1–5]. The recent studies of doped ceria-carbonates composite electrolytes, offering a combination of high ionic conductivity and fuel cell performance, have open the avenue of realizing ceramic fuel cell operating at this low temperature range [6–12]. In addition, a growing interest is attracted to symmetrical fuel cell (SFC)

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[13–18] for its number of advantages, such as high tolerance to sulfur poisoning and carbon deposition, the simpler cell manufacture process and subsequent improved stability and reliability. Currently, the used symmetric electrode materials are perovskite oxides [13,16]. However, most of them suffer from one or several drawbacks: high processing cost, inadequate electrical conductivity both in oxidation and reduction atmospheres, and unsatisfactory electro-catalytic activity as electrode both for oxygen reduction and fuel oxidation even at extreme high temperature, and so on [17]. For example, the perovskite oxide  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  was thought to be the most promising electrode for symmetrical SOFC in the term of its electrical conductivity and catalytic activity [16,18]. It, however, was found to react with water below 800 °C, causing degradation during thermal cycling [19]. Therefore, it is highly desirable to develop novel symmetrical electrode materials for low temperature SFC.

As a continuation of research into the electrode materials for low temperature ceramic fuel cell (LT-CFC) [20–25], in this study, we further choose CuO and ZnO modified lithiated NiO (denoted as LNCZO) as the special electronic component and characterize its electrochemical performance as a symmetrical electrode for ceria-based composite based CFCs. The choice of such composition has the following considerations: Lithiated NiO has been employed as the electrodes for SFC and shows adequate catalytic activity [20]. For the anode, the formation of Cu/Ni alloy can reduce the electrode polarization resistance and enhance the tolerance to carbon deposition [26]. Besides, the Cu/ZnO composite, a commercial methanol steam reforming catalyst, partially fills the requirement of the direct hydrocarbon fueled CFCs [23]. Moreover, the chemically benign and structurally stable n-type semiconductor of ZnO oxide can enhance the dispersion of metal or alloy and thus improve the electrode redox stability [27]. From the cathode aspect, the transition oxide composite was employed as cathode materials for molten carbonate fuel cell [28]. The lithiated NiO have also been demonstrated to show the potentiality for oxygen reduction in low temperature FC [29]. Furthermore, the introduction of the metal oxide solid solution to NiO lattice can effectively improve the oxygen reduction reaction rate and also the dissolution tolerance in molten carbonate [30]. Therefore, integrating with these multi-functionalities, low cost and the novel SFC configuration, it is expected that LNCZO symmetrical electrodes will show promising prospect for low temperature application.

On the other side, though there are several reports on the development of novel electrode for LTCFC, especially the lithiated transition metal oxide composite [21,23], few has examined the electrode catalytic losses in these novel LTCFC systems [22,24,31]. It is unclear why these LTCFC systems performed so well while the catalytic activity of traditional cathodes at these temperatures ( $\leq 600$  °C) is the key barrier for high performance. This work illustrates the potential of lithiated transition metal oxide as potential electrode for ceria-based composite low temperature CFCs by (1) proving high catalytic activity both in air and in reducing atmospheres and (2) identifying the hydrate effect of transition metal oxide using symmetrical cells and by means of impedance spectroscopy in different applied gas atmospheres, i.e. in air, hydrogen gas and humidified air.

## 2. Experimental

Composite electrolyte with the composition of  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (SDC)-(Li/Na) $_2\text{CO}_3$  was prepared as our previous work [10]. LNCZO nanocomposite was synthesized by a solid-state reaction method with  $\text{Li}_2\text{CO}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and ZnO as the raw materials. All the chemicals are analytical grade and purchased from the Guangfu Reagent Company, Tianjin. The molar ratio of Li: Ni: Cu: Zn is 2:2:1:2. The raw materials were first ball milling mixed and subsequently sintered at 700 °C for 180 min to get a blank powder. The sintered sample was then crashed with mortar and pestle and denoted as LNCZO.

X-ray powder diffraction (XRD) patterns were recorded at room temperature on a Philips X'pert pro super Diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). To get the reduced crystal phase, LNCZO was set at 5%  $\text{H}_2$  gas balanced with  $\text{N}_2$  for 10 h.

Two types of cells, electrolyte supported and anode supported fuel cells were fabricated by a dry-pressing process for catalytic activity and fuel cell performance measurements, respectively. The electrode contains LNCZO and electrolyte powder at a weight ratio of 3:2. The silver paste and silver coated Ni-foam were respectively used as the cathode and anodic current collectors. Detailed regarding the fabricated procedure was described in our previous work [10]. To test the catalytic activity of LNCZO, both electrode surfaces of the electrolyte supported cells were exposed to humidified  $\text{H}_2$  through a water bubbler or flowed air at a flowing rate of 80 ml  $\text{min}^{-1}$ , and measured by an electrochemical workstation (PARSTAT 2273, Princeton Applied research, USA).

The anode supported cells were applied to test the I–V characteristics with flowing humidified hydrogen and air as fuel and oxidant, respectively. The hydrogen flow rate was 100–150 ml  $\text{min}^{-1}$  while an air pump from YinHu Company was used to provide ambient air (80–120 ml  $\text{min}^{-1}$ ) directly to the cathode chamber.

AC impedance spectra, recorded at 500, 550 and 600 °C, respectively, were taken with 5 points per decade under open circuit voltage condition. The applied frequency range was 100 KHz–0.1 Hz or 0.01 Hz with an amplitude of 20 mV. A stabilization time of 30 min was considered between each temperature change.

## 3. Results and discussion

The crystal structure of the lithiated transition metal oxide and the hydrogen reduced sample are shown in Fig. 1, the standard diffraction pattern of NiO (PDF No. 73-1519), ZnO (PDF No. 89-0510) and Ni/Cu alloy (PDF No. 65-9048) are also given for identification. In the oxidation state, the oxide is identified to NiO and ZnO respectively. The peaks belonged to CuO and lithium oxide are not observed; both of them may be doped into the crystal lattice of NiO and ZnO to form the solid solution, especially for lithium element that can replace the transition metal site or be set into between two different transition metal ion and/or lattice oxygen because of its smallest ionic radius (0.059 nm). In fact, the diffraction peaks are shifted toward higher angles compared with the standard

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