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Investigation of LiNiCuZn-oxide electrodes prepared by different methods: Synthesis, characterization and properties for ceramic carbonate composite fuel cells

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ABSTRACT

A ceramic carbonate composite fuel cell (CCCFC) is considered as a potential candidate among other fuel cell technologies. Before this technology can be commercialized, cost effective and efficient electrodes are needed. There are various preparation methods to synthesize electrode materials. In this work, two different synthesis methods to produce LiNiCuZn-oxide electrode materials were investigated: a slurry and a conventional solid preparation method. Material properties of the electrode powders were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses and scanning electron microscopy (SEM). Electrochemical impedance spectroscopy was used to study electrochemical properties of the electrode materials in air. For this purpose, symmetric cells were prepared where a mixture of samarium doped ceria and alkali (Li, Na, K) carbonates was used as an electrolyte. It was found that the LiNiCuZn-oxide based electrode materials prepared with the slurry method had smaller particle sizes (10 nm–100 nm vs. 100 nm–1 μm), a larger surface area (17.7 m^2g^{-1} vs. 1.9 m^2g^{-1}) and a higher porosity ($7.0\cdot10^{-2}$ cm^3g^{-1} vs. $6.5\cdot10^{-3}$ cm^3g^{-1}). Furthermore, the cells fabricated using the electrode materials prepared with the slurry method had a lower polarization resistance in air (0.21 Ωcm^2 vs. 0.31 Ωcm^2 at 550 °C).
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Introduction

Composite carbonate-ceramic fuel cells (CCCFCs; operating temperature 300–600 °C) have been developed as a potential source for efficient and clean energy production. CCCFC typically uses a composite mixture of either samarium or gadolinium doped cerium oxide (SDC/GDC) and a mixture of alkali (Li, Na, K) carbonates as the electrolyte material. Both of these compounds can conduct ions, which is different compared to a solid oxide fuel cell (SOFC) and a molten carbonate fuel cell (MCFC) on which the CCCFC is based. In addition to the electrolyte, cost-effective electrodes are needed to achieve high performance fuel cells [1]. Several

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different methods have been reported for electrode layer preparation: powder pressing method [2–5], combustion spray process [6], chemical vapor deposition [7], sputtering [8], screen printing [9], ink-jet printing [10] etc. The size of the electrode material, which is dependent on its synthesis method, affects its electrochemical performance. Various synthesis methods have been reported for preparing the electrode materials, such as a slurry or co-precipitation method [5], an electrospinning and Pechini process [11], a solid state method [12] and a sol–gel method [13]. These methods greatly affect the performance of the electrodes and thus it is important to perform a comparative study on potential electrode preparation methods to analyze their impact on the CCCFC performance.

In previous works, LiNiCuZn-oxide based electrodes have been developed as promising electrode materials for CCCFC [4,5]. However, the effect of different synthesis methods, especially on the particle size, is still not thoroughly understood and needs more clarification. For this reason in this work, two different potential electrode preparation methods, a slurry method and a conventional solid (state) method, have been used to prepare LiNiCuZn-oxide based electrode materials of different particle sizes. Their potential performance as CCCFC electrodes was studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses. Additionally, symmetric cells were manufactured from these materials and characterized in air using electrochemical impedance spectroscopy (EIS). According to the results, the slurry method is a more promising way to produce electrode materials for CCCFCs.

Experimental

Material preparation

Nickel and lithiated nickel oxide have long been used as catalysts in high temperature fuel cells [1]. Copper on the other hand, shows a good resistance against carbon deposition when hydrocarbon fuels are used [14] and an addition of copper oxide has increased the catalytic performance of the nickel based electrodes [15]. Similarly, an addition of zinc oxide has been noted to enhance the catalytic performance of the electrodes [16] and also to decrease the solubility of nickel oxide into carbonate melts [17]. The latter property is especially important when doped ceria/carbonate mixture is used as an electrolyte.

Two different methods were used for preparing LiNiCuZn-oxide based materials: a slurry preparation method and a conventional solid preparation method. These materials acted as electrode precursors and were characterized in various experiments. The precursors were also mixed with electrolyte and pore formers before being used in electrochemical experiments as is explained later. All the chemicals were purchased from Sigma Aldrich.

In the slurry method, $LiNO_3$ (2.07 g), $NiCO_3 \cdot 2Ni(OH)_2 \cdot xH_2O$ (16.4 g), $CuCO_3 \cdot Cu(OH)_2$ (5.3 g), $[ZnCO_3]_2 \cdot [Zn(OH)_2]_3$ (8.4 g) and citric acid (10.5 g) were mixed in deionized water. The liquid was then evaporated while being stirred on a hotplate at around 100 °C. Afterwards, the remaining slurry-like mixture was first heated in an oven at 400 °C for 1 hour in order to remove carbon based materials and then calcined at 700 °C for 1 hour to produce metal oxides. Finally, the mixture was ground in a mortar for half an hour.

Table 1 – Material compositions of slurry and solid electrodes. The weights of the materials are compared to the weight of the electrolyte.

	Solid	Slurry
Precursor	1.20	1.08
Electrolyte	1.00	1.00
Li_2CO_3	–	0.12
Ethyl cellulose	0.15	0.15

For the conventional solid method, $NiCO_3 \cdot 2Ni(OH)_2 \cdot xH_2O$ and $Cu(NO_3)_2 \cdot 2½H_2O$ were first calcined separately in an oven at 900 °C for 2 h in order to obtain nickel and copper oxides. NiO (5 g), CuO (1.565 g), ZnO (2.565 g) and Li_2CO_3 (1.09 g) were then ground together in a mortar, calcined at 600 °C for 1 h and ground again for half an hour.

A mixture of $(Li_{0.44}Na_{0.29}K_{0.27})_2CO_3$ and $Ce_{0.8}Sm_{0.2}O_{1.9}$ was used as an electrolyte material (abbreviated as LiNaK-SDC; carbonate to SDC weight ratio was 30:70). Nanosized LiNaK-SDC was prepared via a freeze drying method similarly to the method in Ref. [18]. Briefly, $Ce(NO_3)_3$ and $Sm(NO_3)_3$ were first dissolved into deionized water. Citric acid was then added to the solution (the molar ratio of Ce + Sm to citric acid was 1:2) after which ammonia was added until the pH of the solution reached 10. Carbonates were mixed into the solution according to their molar and weight ratios and finally, polyethylene glycol was added to the solution (the weight ratio of $Ce(NO_3)_3$ + $Sm(NO_3)_3$ to polyglycol was 1.75:1). The mixture was then stirred vigorously, freeze dried for 24 h and calcined at 800 °C for 1.5 h.

Material characterization

The crystal structure of the electrode precursor materials was measured using an XRD unit (PANalytical X'Pert PRO MPD).

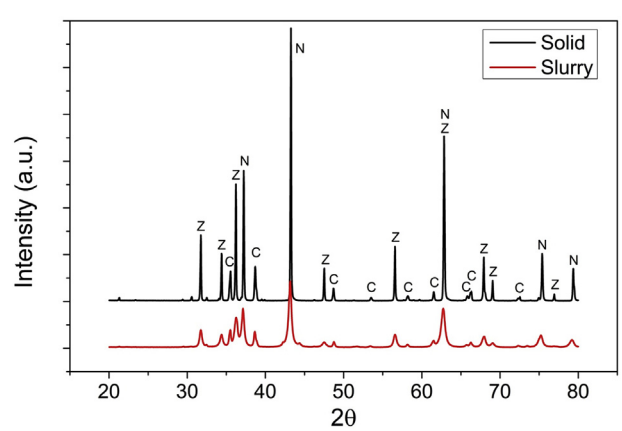

Fig. 1 – XRD graphs of the precursor samples. Z, C and N correspond to ZnO, CuO and NiO phases, respectively.

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