

Preparation and application of LiSiC-oxide for low temperature solid oxide fuel cells

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Semiconductors are well known as excellent materials in the field of exploring novel avenues which combine various fields in electronics, electrochemistry, etc for new functional device concepts. Lithium silicon carbide (LiSiC) is a well-known electrode material for Lithium ion batteries but relatively new for solid oxide fuel cells (SOFCs) and electrolyte-layer free fuel cells (EFFCs). In the present work, we have explored three categories of fuel cells based on mixed LiSiC-SDC (samarium doped ceria) in SOFC and LiSiC as a single component material with type (I) and without coating of a layer of 3C-SiC as EFFC type (II). All of three cells are sandwiched between Ni foams coated with NCAL ($\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{Li}$ -oxide). The electrochemical performances of as prepared fuel cells are tested at 550°C, which is substantially lower than in conventional fuel cell materials. The LiSiC based EFFC type (II) demonstrates better performance because of less ohmic resistance as compared to type (I) have more layers. This indicates that the LiSiC-SDC system has potential for fuel cell development in accordance with energy band structure and alignment.

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1. Introduction

There is an urgent need to explore various novel sustainable energy resources to handle the overbearing needs of global energy required for the growing society. As new avenue in electronics and electrochemistry, the solid oxide fuel cell (SOFC) technology appears with several advantages that can lead to high efficiency, extremely low toxicity, tremendous fuel flexibility, etc. [1]. The research discoveries of the properties in the material system can pave the way towards commercialization of this technology [1-5]. However, at the early stage there are costs to be considered regarding high temperature operation and manufacturing of the conventional materials which are associated with sophisticated material preparation processes and critical material selection if such should be viable to reach an application stage [6]. The key prerequisite of high temperature is inevitable for fuel cell functioning as it provides high ion conductivity and fast electrode reaction kinetics. At the same time, it is at disposal of instability induced in devices due to degradation effects [6, 7]. Conversely, lowering the working temperature of SOFCs improves the thermal stability and reduces the material costs due to availability of variety of material [8].

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The underlying basic mechanism of fuel cell technology relies upon power density and ionic conductivity. A lower temperature begins to influence these complications and is challenged by a lower performance that will discourage to develop applications. This is a motivation to explore novel materials which may lead to stable conductivity at lower temperature and thermal mechanical stability.

Research initiatives have emerged to develop new semiconducting and ionic compositions for SOFCs. Some examples are YSZ, GDC anodes and ceramic oxide cathodes which substitute ionic carbonates (Li_2CO_3 , Na_2CO_3 , K_2CO_3) with metal oxides [9, 10]. The explored materials show better electrochemical performance and ionic conduction as compared to conventional electrolytes. Promising results of Li-ZnO and SDC electrolyte has demonstrated great ionic conductivity and power density up to 600 mW/cm^2 [11]. There have been reports of heterostructured electrolyte materials such as LiNiZn-oxide [12-14]. The EFFC (electrolyte-layer free fuel cell) or SIMFC (semiconductor ionic membrane fuel cell) may pave the way to explore electronics and electrolyte understanding with integration of concept of Schottky junction effect based on energy band alignment similar to perovskite solar cell principles [12, 15-17]. This approach motivates us to combine these mechanisms in our LiSiC-SDC composite material concept. The manufacturing of EFFC becomes simpler since one component structure is applied as compared to three component structures.

Silicon based materials such as Si, SiO_2 and SiC are extensively applied as electrode materials. A Si based SOFC in nanosize thickness films in YSZ electrolyte demonstrated a peak power density of 317 mW/cm^2 at 400°C [18]. Bin Zhu et al. observed that SiO_2 in natural hematite-LCP based composites reached a peak power density of 467 mW/cm^2 at 600°C as effect of enhanced interfacial conduction at grain boundaries [4, 19, 20]. Combinations such as $\text{SiO}_2/\text{Fe}_2\text{O}_3$ and LCP/ SiO_2 with Silicon Carbide (SiC) have higher thermal conductivity [21]. These have also a stable chemical and mechanical structure. It showed promising performance as a catalyst support in PEM fuel cells, low temperature fuel cells and in photocatalysis for hydrogen production [22, 23]. It is reported that optoelectronic properties of this material is enhanced by creation of vacancies of oxygen that may play the role of enhanced ionic conduction in case of SOFCs and EFFCs [24]. It is already explained in our perspective article on possible advantages of SiC in EFFCs that it may play a role in reducing activation energy of the EFFC due to fast heat transportation to overcome internal resistance of the device and enhance ion transportation [25]. So, here is an understanding from thermal conductivity and mechanical stability perspective that using 3C-SiC may enhance the performance of the device and it leads to a better thermal connection between the electrolyte and electrodes since it improves the capacity of LiSiC-oxide as an electrode material [26]. In this study, we report two types of fuel cells based on LiSiC-SDC as SOFC and LiSiC based EFFC, sandwiched between NCAL pasted Ni-foam layers. There is introduced a concept of ceramic coating to enhance the thermal and mechanical stability so one EFFC is with and one is without coating of 3C-SiC layer on top of the cells. All cells are tested for electrochemical performance at 550°C . LiSiC composites based EFFC with a buffer layer of 3C-SiC showed better results.

2. Experimental section

2.1. Material synthesis

The LiSiC-oxide was prepared by a slurry method in two steps. In the first step, commercially purchased 3C-SiC powder was sintered for 2 hours at 650°C to obtain a more fine grains structure of the material. The obtained powder was thoroughly grounded in a mortar with a pestle for further use in preparing composition of electrolytes for three fuel cell devices. In the second step, commercially purchased Li_2CO_3 and heat treated 3C-SiC powders were mixed at a weight ratio of 1:1. The mixture of above two compounds was dissolved into an appropriate amount of 10 ml of HNO_3 solution with stirring and heating at 150°C for 1 hour to form sol type slurry. The slurry was then sintered at 800°C for 2 hours to obtain final product. The resulting product was then grounded again to obtain homogenous LiSiC-oxide material for further use.

The commercial 3C-SiC was purchased from Hongwu International Group, China and raw Li_2CO_3 was purchased from a rare-earth metals and ceramics company in Batou, China. The $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{Li}$ -oxide (NCAL) was also purchased from Tianjin Bamo Science and Technology, China. The NCAL was mixed in a solvent terpineol to form a slurry mixture that was convenient to paste it onto Ni-foam in order to use as an electrode.

2.2. Fuel cell fabrication

Three fuel cell devices were fabricated based on the prepared LiSiC composite. Firstly, three layers of LiSiC-SDC-LiSiC were assembled in respective order between two layers of Ni-foam pasted with $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{Li}$ -oxide NCAL as a current collector and enhancement of electrode activity. The final product in form of a tablet was obtained through an application of load of 220 MPa. The resultant pellet was 13 mm in diameter and thickness of 2 mm. The effective area of cell was measured about 0.64 cm^2 . Second device was fabricated by sandwiching LiSiC between two layers of Ni-foam pasted with NCAL without any coating of 3C-SiC. The third device was fabricated similar as the second device and an additional coating of 3C-SiC on top. The electrochemical performance measurements for fuel cells were carried out on a programmable electronic load instrument (IT8511, ITECH Electrical Co., Ltd., Nanjing, China) at $550\text{ }^\circ\text{C}$ with humidified hydrogen as fuel (80–120 ml/min) and air as an oxidant (80–120 ml/min). The configuration of the three devices is shown in Fig. 1.

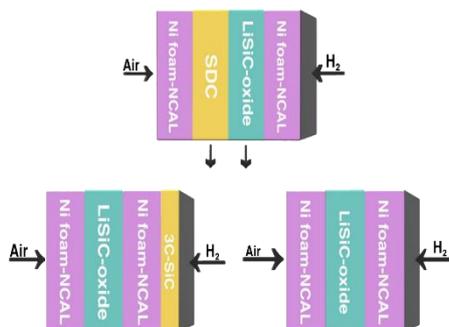


Fig. 1. Configuration of the three devices.

The powder X-ray diffraction pattern of prepared sample were analyzed by using a Bruker D8 Advanced X-ray diffractometer with source of $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{ \AA}$) with tube voltage at 45 kV and current of 40 mA. The particle morphology and microstructure of the powder samples were investigated using a JSM-7600F field emission scanning electron microscope (FESEM, Japan) operating at 15 kV. The optical properties of commercial 3C-SiC were studied before the preparation of functional material by using Cary 60 UV-Vis – Agilent under the operating conditions of Double Beam wavelength range of 190–800 nm with a resolution of 1.5 nm and light source based on Xenon flash lamp (80 Hz). The measurement of electrical conductivity of commercial 3C-SiC powder was performed on a DC 4 probe station (K22531) digital micro-ohm meter. The powder was compressed into form a pellet found with an effective area of 0.64 cm^2 and thickness of 5mm under a pressure of 210 MPa. As a current collector, slurry of Ag paste was coated on both circular faces of the pellet for measurement of electrical conductivity. The V-I measurement of commercial 3C-SiC powder was also recorded by using a 4 point probe vacuum system (ChangMin, LTD, CMT-SR2000N).

The electrochemical performance including open-circuit voltage (OCV) and V-I, P-I curves were analyzed on a programmable electronic load instrument (IT8511, ITECH Electrical co.,Ltd Nanjing, China) at $550\text{ }^\circ\text{C}$. The measurements were carried out by attaching the samples to a temperature controlled thermocouple inside a temperature controlled tube furnace. The resulting current and power densities were recorded by varying the external electronic resistance that decreased the cells voltage by 0.05 V from the OCV. The flow meter (LZBF-50) Tianjin Liuliang Yibiao Youxian Gongsj, China was used to control the flow of pure Hydrogen at 80 ml/min to the

fuel electrode. An identical amount of air as an oxidant was pumped by a gas pump (SL-2800, YinHu Ltd, China) to the oxygen electrode.

3. Results and discussion

3.1. Crystalline structure and morphology

The XRD spectrum of the commercial 3C-SiC is presented in Figure 2. The XRD pattern of the powder shows a series of characteristic diffraction peaks that correspond to the (111), (200), (220) and (311) planes in JCPDS card reader 29-1129, these values match with the peaks of cubic structure of 3C-SiC. According to the Scherrer equation $D = K\lambda / \beta \cos\theta$, the average grain size (D) of the material is calculated as 58 nm. The interplanar spacing D and lattice parameters of 3C-SiC are also calculated from the XRD data.

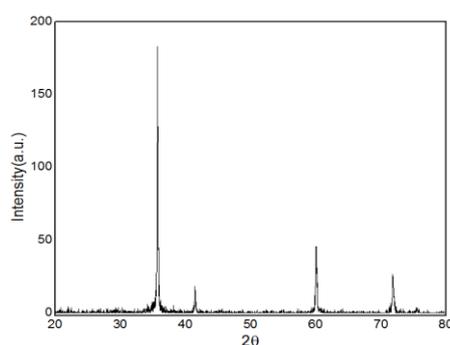


Fig. 2. XRD pattern of 3C-SiC.

The microstructure of the commercial 3C-SiC was analysed through SEM. Figure 3(a, b) shows the morphology of the 3C-SiC particles. The 3C-SiC material exhibits irregular shaped particles. The reason of the irregularity can be due to the manufacturing process that gives a range of particle size. Moreover, the average particle size is larger than the XRD analysis calculated by Scherrer equation. The SEM analysis also indicates that the smaller grains are transformed to larger particles due to agglomeration.

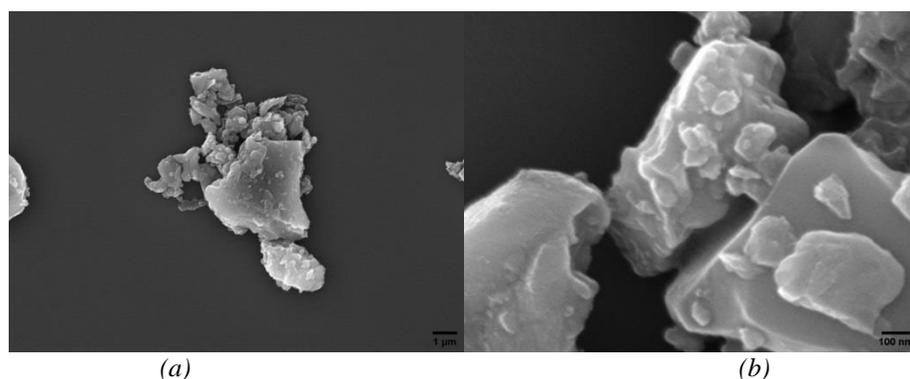


Fig. 3. SEM of 3C-SiC at (a) micro level (b) nano level.

3.2. UV-visible spectroscopy

For an electrolyte material, the exploration of energy band level is used to understand the working of SOFC and EFFC devices. The UV-visible spectra of the commercial 3C-SiC were measured to obtain the band gap of the material as a function of wavelength in the spectral range

from 300 to 800 nm, and are shown in Fig. 4(a, b). The bandgap of the material is calculated as 2.3 eV by using the following equation.

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

This is similar to the 3C-SiC single crystal material. Thus the grains are expected to have single crystal electronic 3C-SiC character. These findings may help to illustrate the normal working of devices based on 3C-SiC to enhance the electrochemical performance by electron blocking through concept of energy band alignment. The optical study helps to understand the required energy levels to separate electron and holes to avoid short-circuiting of the device and its enhanced electrochemical performance [27, 28].

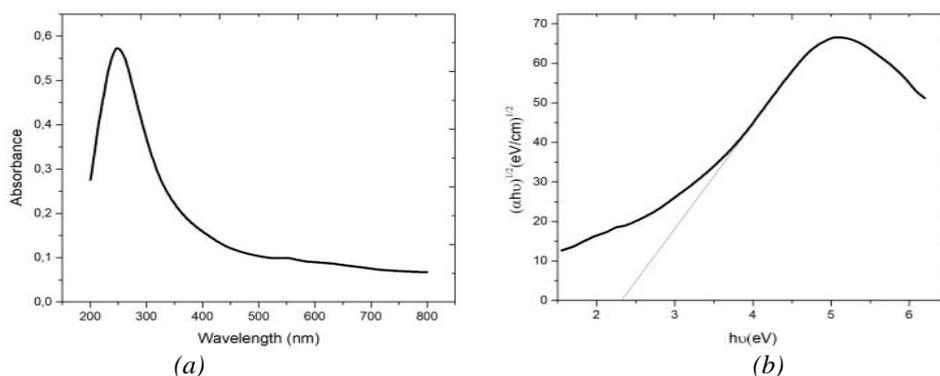


Fig. 4. (a) UV-Vis absorbance spectra, (b) Tauc plot of 3C-SiC.

3.3. Electrical characterization

3.3.1. Electrical conductivity

Electrical conductivity of used material 3C-SiC is measured under air conditions as shown in Fig. 5. The measurement suggests that electrical conductivity remains linearly constant for a long range of temperature and there is no increase or decrease of conductivity with rising temperature. The trend of temperature dependent conductivity followed by this material may be due to the fact that it's a commercial material with defects that hinders an increase in conduction as previously low conductivity is reported for commercial material as compared to lab synthesized ones. As the bandgap of 3C-SiC is 2.3 eV. There is no expected conductivity at this temperature range since there is no excitation from valence to conduction band. This behavior of 3C-SiC has motivated us about the stability of fuel cells using this material [29]

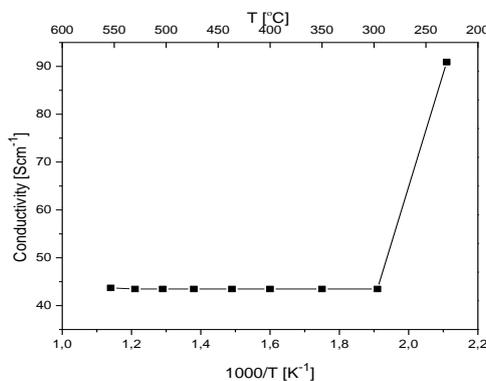


Fig. 5 Temperature dependent conductivity measurement of commercial 3C-SiC.

3.3.2. IV Characteristics

The IV response curve of the commercial 3C-SiC under biased voltage is shown in Figure 6. This study is performed with removable graphene contacts shows the comparison of I-V characteristics at room temperature. The graphene enhanced the electrical measurements to mA at 5 volt. There is clear demonstration of rectification response under measurements performed with contact. This response further elaborates the formation of junction effect under biased voltage that is already reported [30] to establish an electron blocking layer to enhance electrochemical performance of functional materials.

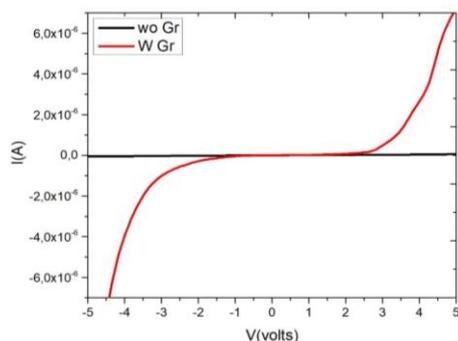


Fig. 6. I-V characteristics of commercial 3C-SiC.

3.4. Electrochemical performance

Fig. 7(a) shows the performance of the fuel cell based on the working principle of SOFC device with LiSiC-SDC as an electrolyte sandwiched between two Ni-foam pasted with $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{Li}$ -oxide (NCAL). Fig. 7(a) shows typical current-voltage (I-V) and current-power (I-P) characteristics of SOFC fuel cell based on LiSiC-SDC measured in fuel cell conditions at 550 °C. It can be observed that three components fuel cell with a structure LiSiC-SDC-LiSiC delivers an OCV (open circuit voltage) of 0.85 V and a maximum power density of 75 mW cm^{-2} . This is the first demonstration of 3C-SiC material in a fuel cell device that shows considerable performance at low temperature. It reveals a potential of 3C-SiC associated with scientific and technological as well as applied perspectives for electrolyte uses. We also note that the performance is comparable to that of already reported direct carbon fuel cell based on SnO_2/SDC (Sm-doped CeO_2) as an extra anode layer electrolyte, and even superior to some other SOFCs (solid oxide fuel cells) using ceria-based electrolytes[31, 32].

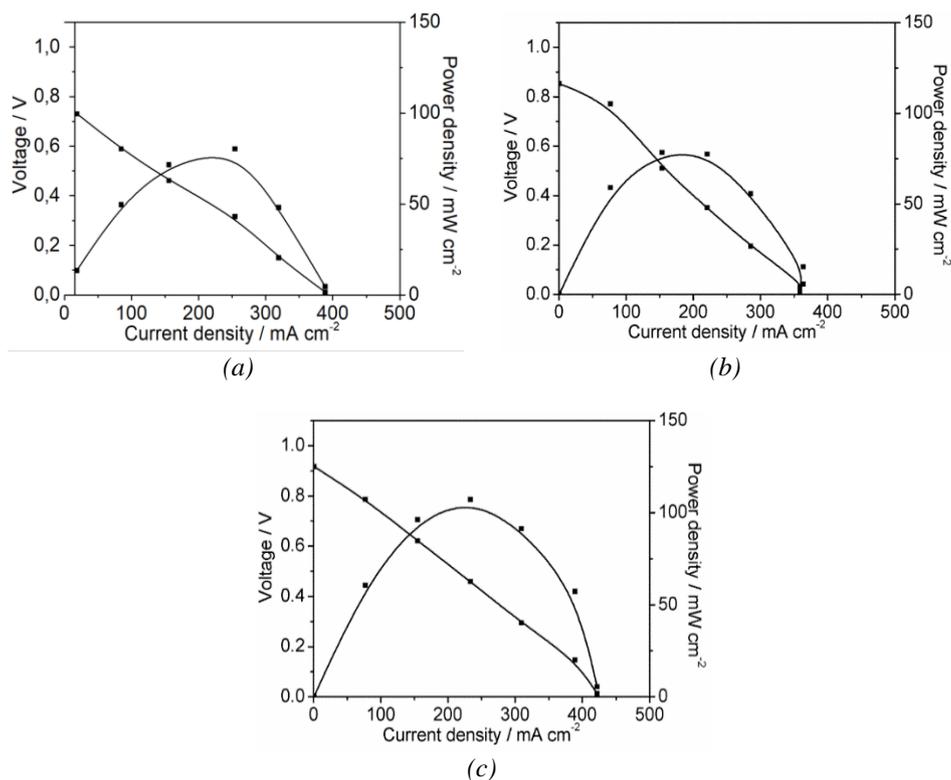


Fig. 7. (a,b,c) Electrochemical performance of fuel cell based on LiSiC-SDC-LiSiC and LiSiC based EFFC TYPE I and TYPE II.

The LiSiC-oxide based fuel cell was explored with modifications (with and without 3C-SiC) in device structure at same temperature of 550°C. Fig. 7(b) shows the performance of EFFC device (type I) based on LiSiC-oxide as a single component. From electrochemical performance, these investigations lead to the idea to further assessment of the EFFC device based upon LiSiC-oxide by introducing a thin layer of 3C-SiC on top of the cell EFFC (type II). The performance is shown in Fig. 7(c). This modification in the structure of device results into a boosted power output from 75 mW/cm² to 120 mW/cm² as shown in Fig. 7(c). The values of OCV are seen to be fluctuating between 0.8 V to 0.9 V in all of three cells. The high values of OCV can be associated to the temperature of 550°C that is high enough for thermal activation and transportation of ions across the devices. Another reason behind the raised OCVs is the catalytic activity of NCAL that is pasted on Ni-foam. There is also reported the effect of Schottky junction formed during reduction reaction between the electrolyte and NCAL due to formation of metallic alloy at anode side of the devices [16] This junction effect plays a role of a barrier for electrons from passing through the device from the side of H₂ supply. Reason behind the enhanced performance of LiSiC-oxide based EFFC (type II) device may be attributed to distinguished properties of 3C-SiC to reinforce thermal and mechanical stability of the structure. It may have played double role as a ceramic support and its semiconducting characteristics by enhancing electrochemical performance as compared to pure ionic electrolytes. Consequently, there is a significant electronic conduction in the LiSiC-based electrolytes, high OCVs can still be obtained by the cells with further modifications. However, it still can be concluded from current initial results that both LiSiC-SDC-LiSiC as a conventional fuel cell and LiSiC as an EFFC can function well as functional materials in low temperature SOFCs. These are the preliminary results of fuel cells with 3C-SiC, which could be further improved with future research works.

4. Conclusion

In summary, three LiSiC-oxide based devices have been developed for low temperature SOFCs applications for the first time. Out of three types of fuel cells based on synthesis of LiSiC composites, one has exhibited considerable power output at low temperature of 550 °C. The improvements in electrochemical performance are to be majorly owing to reduced activation energy and higher thermal conductivity of developed composite material. These findings recommend that LiSiC-oxide based composites are attractive materials for developing new functional membranes for low temperature SOFCs.

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