Intermediate temperature fuel cells based on doped ceria–LiCl–SrCl₂ composite electrolyte

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Abstract

A new type of oxide-salt composite electrolyte, gadolinium-doped ceria (GDC)–LiCl–SrCl₂, was developed and demonstrated its promising use for intermediate temperature (400–700 °C) fuel cells (ITFCs). The dc electrical conductivity of this composite electrolyte ($0.09-0.13$ S cm^{-1} at $500-650$ °C) was 3–10 times higher than that of the pure GDC electrolyte, indicating remarkable proton or oxygen ion conduction existing in the LiCl–SrCl₂ chloride salts or at the interface between GDC and the chloride salts. Using this composite electrolyte, peak power densities of 260 and 510 mW cm^{-2}, with current densities of 650 and 1250 mA cm^{-2} were achieved at 550 and 625 °C, respectively. This makes the new material a good candidate electrolyte for future low-cost ITFCs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: GDC–LiCl–SrCl₂; Composite electrolyte; Intermediate temperature fuel cells; Electrical conductivity

1. Introduction

Fuel cells (FCs) are relatively benign, highly efficient devices that convert chemical energy of fuel and oxidant gases directly into electrical energy while causing little pollution [1]. High temperature fuel cells such as solid oxide fuel cells (SOFCs), which use yttria stabilized zirconia (YSZ) as electrolyte usually have high fuel flexibility and do not need expensive catalysts such as platinum. However, in current SOFC stack constructions the high operating temperature (∼1000 °C), at which the YSZ electrolyte has sufficient oxygen ion conductivity, results in other problems, e.g. (i) the difficulty in sealing is increased; (ii) chemical stability of the FC components are more critical. These disadvantages hindered the SOFCs commercialization. Consequently, great efforts have been taken to reduce the operating temperature of SOFCs in recent years. Two methods have been used to decrease the operating temperature. One is to reduce the thickness of the electrolytes, i.e. using film electrolytes [2–4]. However, this method usually requires rather difficult preparation technique and hence raises the fabrication cost. The other is to find alternative electrolytes that have much higher ionic conductivity than YSZ at intermediate temperature range. Doped ceria is a good choice and is being widely investigated [5,6].

Some other materials had also been attempted to be used as electrolytes for ITFCs, such as the salt-oxide composite materials. Zhu and co-workers studied the oxyacid salt-oxide composite electrolyte [7–10]. Most work for oxyacid salt-oxide composite was focused on sulphate–alumina. A typical example is Li₂SO₄–Al₂O₃ system. This material has high proton conductivity in hydrogen-containing atmosphere. However, it was discovered that Li₂SO₄ is chemically unstable in hydrogen atmosphere, resulting in poor stability for H₂/O₂ fuel cell [11].

Tao and Meng [12] first found that NaCl has both proton and oxygen ion conduction. The H₂/O₂ fuel cell using NaCl–Al₂O₃ as composite electrolyte and platinum as both electrodes showed a maximum current density of 140 mA cm^{-2} at 720 °C. That work implies that other chlorides may also have proton or oxygen ion conduction and may be used as the electrolyte for fuel cells. By replacing the insulating phase, Al₂O₃, with the highly conducting phase, rare-earth-doped ceria, it is possible to develop new doped ceria-chlorides composite electrolyte which should have high electrical conductivity at intermediate temperature range. Compared with the pure rare-earth-doped ceria (such GDC), this composite electrolyte can reduce the use level of the rare-earth element so as to reduce the cost. Another advantage

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is the possibility of finding much more highly conducting composite electrolyte than pure doped ceria by carefully selecting the chlorides, for instance, to adopt the low-melting point chlorides.

In this paper, we have developed a new doped ceria–LiCl–SrCl$_2$ composite electrolyte and demonstrated its promising use for ITFCs. Good chemical stability and high fuel cell performance at intermediate temperature make it an attractive candidate electrolyte for future ITFCs.

2. Experimental

2.1. Preparation of composite electrolytes and electrodes

The powder of gadolinium-doped ceria (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$, GDC) was prepared by oxalic acid coprecipitation method as described elsewhere [13]. The rare-earth nitrates, oxalic acid and ammonia used here are all analytical reagents purchased from Shanghai Chemical Corp. The LiCl·H$_2$O (AR, Shanghai Chemical Corp.) and SrCl$_2$·6H$_2$O (AR, Shanghai Chemical Corp.) (molar ratio 1:1) were first dissolved in alcohol (>99.7%). Then the GDC powder and appropriate amount of acetone were added into the mixture followed by thoroughly grinding. The weight ratio between GDC powder and chloride (containing crystalline water) was 12:5. The volume of the liquid phase (acetone and alcohol) was two times more than that of the solid phase. After grinding, the slurry was dried and then calcined at 600 °C in air for 1 h. The as-prepared powder was used as the composite electrolyte.

The composite anode powder was the mixture of NiO and GDC (40:60 weight ratio). The cathode powder was LiNiO$_2$ prepared by solid state reaction of LiOH and NiO at 750 °C for 6 h.

The powder XRD patterns of the composite electrolyte were recorded at room temperature using a D/Maxra X diffractometer that employs Cu Kα radiation. The thermal property measurements were carried out using TG (WRT-3) and DTA (CRY-2) with a heating rate of 10 °C min^{-1}.

2.2. Single fuel cell construction and evaluation

Composite electrodes supported fuel cells were constructed. The powders of composite anode, composite electrolyte and cathode were put into a stainless-steel die layer by layer and then were pressed in one step at a pressure of 200–300 MPa. The as-prepared tablet was then heat-treated at 600 °C for 1 h to complete the construction of a single FC. The three layers of anode, electrolyte and cathode were about 0.3, 0.3–0.5 and 0.5 mm in thickness, respectively. Hitachi X-650 scanning electron microscope was used to observe the microstructure of the fuel cell components. The FC assemblies were mounted into the FC device with the following configuration:

$$(H_2 + 3\% H_2O) \text{ anode/electrolyte/cathode} (O_2)$$

The cell size was normally 13 mm in diameter and the active electrode area was about 0.66 cm^2. Stainless-steel was applied as the bipolar plate and silver glue was used as the sealant. The gas flows were normally controlled at around 50 ml min^{-1} under 1 atm pressure. About 3% H$_2$O was added to the H$_2$ fuel gas before feeding to the anode chamber.

Fuel cell *I–V* characteristics were determined by monitoring the current and terminal voltage under variable loads with a computerized data acquisition equipment. The measurements were carried out at 500–650 °C. Through linear-fitting the Ohmic polarization part of the *I–V* characteristics, the total conductivity of the fuel cell electrolyte can be obtained in subtraction of the influence of the electrodes and electrolyte/electrode interfaces as described by Zhu [14].

3. Results and discussion

3.1. Phase and thermal analysis

Fig. 1 shows the powder X-ray diffraction pattern of the composite electrolyte GDC–LiCl–SrCl$_2$. For comparison, the XRD pattern of a single GDC sample was also shown. It can be seen no peak for crystalline salt phase appears in this pattern, which means the salt of LiCl–SrCl$_2$ becomes amorphous after thoroughly grinding and heat treatment. The well-dispersed salt in the composite electrolyte is assumed to provide a better electrical conduction path, which will be discussed afterwards.

To demonstrate the phase composition of the composite electrolyte, TG–DTA was performed, as shown in Fig. 2. Curves (a) and (b) are the TG and DTA curve of GDC–LiCl–SrCl$_2$ composite powder, respectively. For the purpose of comparison, the DTA measurement of LiCl–SrCl$_2$ composite salt, which was mixed with the same proportion as in the GDC–LiCl–SrCl$_2$ composite and melted to form a eutectic, was also conducted, as indicated by curve (c). It can be seen that curve (b) is almost identical to curve (c). The two step weight losses in curve (a) correspond to the two sets of
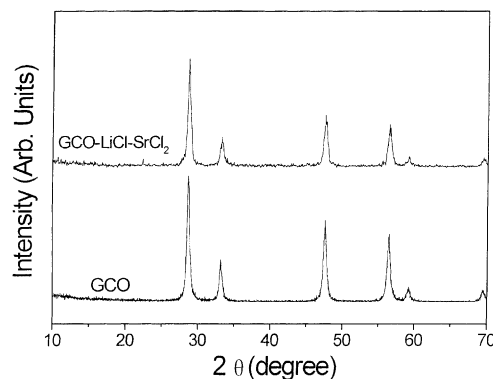

Fig. 1. Powder X-ray diffraction patterns for GDC and GDC–LiCl–SrCl$_2$ composite at room temperature.
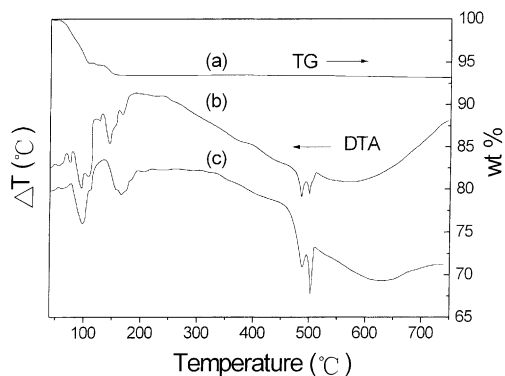
Fig. 2. Thermogravimetry (TG) plot for GDC–LiCl–SrCl$_2$ composite (a) and differential thermal analysis (DTA) plots for GDC–LiCl–SrCl$_2$ (b) and LiCl–SrCl$_2$ (c) in air.

Fig. 3. Phase diagram of LiCl–SrCl$_2$ binary system [15].

endothermic peaks under 200 °C in curve (b). There were approximately 5 and 2% mass losses in these two steps, respectively. The first set of endothermic peaks at about 100–130 °C is attributed to the loss of absorbed water and part of crystalline water in LiCl·H$_2$O and SrCl$_2$·6H$_2$O. The second set of peaks at about 150–180 °C was attributed to further crystalline water loss. Another two endothermic peaks at about 488 and 501 °C in curve (b) have no corresponding weight losses in curve (a), therefore it must be due to the melt of the LiCl–SrCl$_2$ eutectic. Fig. 3 is the phase diagram of LiCl–SrCl$_2$ binary system [15]. It is evident that a eutectic point exists at about 485 °C. This is in consistent with the endothermic peak at about 488 °C in curves (b) and (c). The peak at about 501 °C in curves (b) and (c) is caused by the composition deviation from the eutectic composition (53 mol% LiCl–47 mol% SrCl$_2$). The identity of curves (b) and (c) indicates that the composite electrolyte does contain the amorphous LiCl–SrCl$_2$ eutectic and no reaction occurs between the salt and GDC.
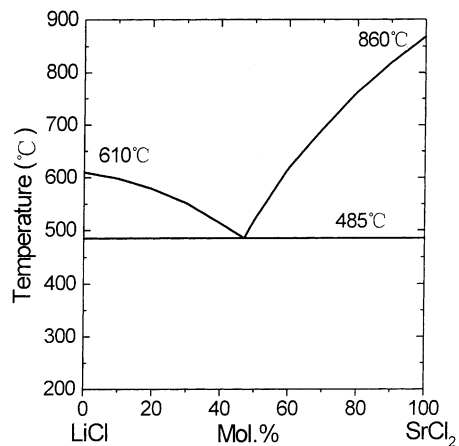
3.2. Microstructure observation

Pure GDC powder prepared by the oxalic acid coprecipitation method was pressed into tablets and sintered at 600 °C for 1 h and then observe its microstructure with SEM, as shown in Fig. 4(a). It was found that the GDC particles prepared by the coprecipitation method are in needle shape with the diameter about 1 μm and length about 2−4 μm. Fig. 4(b) shows the SEM photograph of the composite electrolyte layer of the sandwich-structured single cell, which was also sintered at 600 °C for 1 h before the SEM observation. It is evident that the needle-shaped particles are GDC particles. However, the salt phase in Fig. 4(b) is not very easy to identify. Some ball-shaped particles with the diameter of 0.5–1.0 μm may be identified as the salt particles, but most salts are supposed to be spread on the surface of GDC particles in amorphous state.

Some pores can be seen in the electrolyte from Fig. 4(b), which means the composite electrolyte may be not very
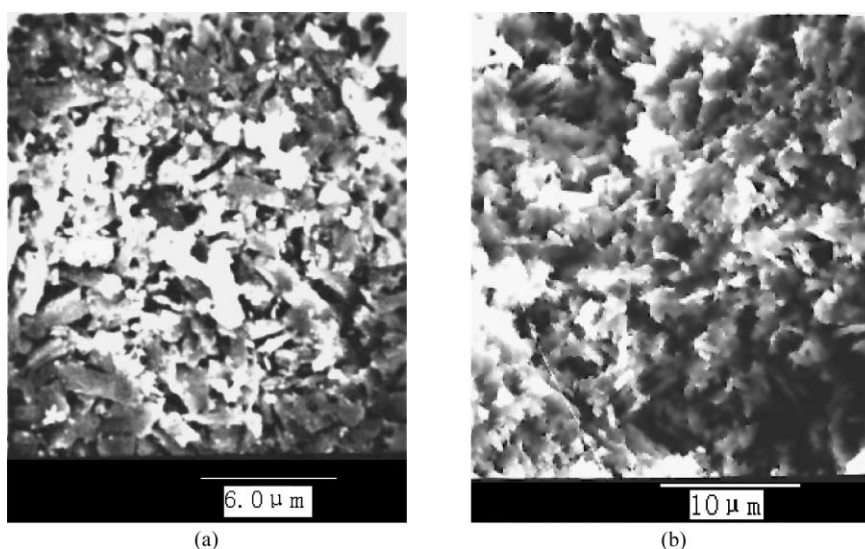

(a)

(b)

Fig. 4. SEM micrographs of pure GDC tablet (a) and GDC–LiCl–SrCl$_2$ composite electrolyte layer in the single fuel cell calcined at 600 °C (b).

gas-tight while the fuel cell is practically in operation, which will lower the open circuit voltage (OCV) as will be shown in Section 3.3. The deposited pores in the composite electrolyte may be due to the low sintering temperature ($\sim$600 °C) and poor chemical and mechanical compatibility of salt with GDC ceramic oxide. In fact, the pressed pellets of pure GDC need at least 1400 °C to be sintered. However, after adding salt into GDC ceramic, it is impossible to sinter at such a high temperature due to the irreversible vaporization loss of the salt phase. Further work is being conducted on increasing the density of the electrolyte by applying new methods.

3.3. Fuel cell performance and electrical conductivity

Fig. 5 shows typical fuel cell I–V and I–P characteristics at various temperatures. The anode, electrolyte and cathode layer of the single cell has the thickness of 0.20, 0.25 and 0.50 mm, respectively. The OCV is about 0.83–0.85 V at 550–625 °C. This value is lower than the theoretical value (1.1–1.2 V) at this temperature range. Supposedly, at least two factors are responsible for the low OCV. One is the partial electronic conduction in the GDC that caused internal short circuit [5,16,17]. The OCV of H_2/O_2 fuel cell using pure GDC electrolyte is usually lower than 0.90 V at 550–650 °C. The other important factor is the gas leakage through the not fully densified electrolyte, which was discussed in Section 3.2. Although the OCV is not very high, it still exhibits relatively high current and power density output. The peak power density could reach 260, 330 and 510 mW cm^{-2} at a current density of 650, 880 and 1250 mA cm^{-2} at 550, 590 and 625 °C, respectively. It is reasonable to believe that improving the preparation technique to make the composite electrolyte fully densified can increase the OCV and hence dramatically improve the fuel cell performance as the peak power density is proportional to the square of the OCV.

The fuel cell's long-term discharging stability was preliminarily examined. We observed that it had discharged at a power density of about 350 mW cm^{-2} at 600 °C for at least 10 h. During the discharging process, some extent of degradation was observed (the power density decreased fr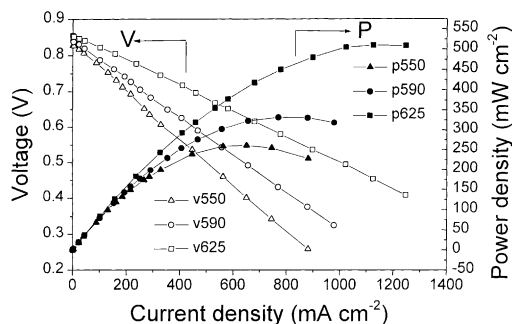om 377 to 352 mW cm^{-2} after 9 h of operation), but it was then automatically recovered (without any artificial interruption) to its initial level 1 h later. The reason for this automatic recovery is not clear yet, although it was assumed to relate to the creeping nature of the molten salt. The recoverable discharging process for so long a time indicates at least that no severe chemical reactions happened between chloride salt and its ambient gases during the discharging process, which is in accordance with the thermodynamic prediction of those alkaline chlorides as described elsewhere [18]. In contrast, the fuel cells using Li_2SO_4-containing electrolyte showed very poor stability and could not discharge steadily for even half an hour [11], which was due to severe chemical reaction between Li_2SO_4 and H_2, as predicted thermodynamically [18]. However, many factors affect a fuel cell's long-term stability. For instance, the evaporation loss of such chlorides may be non-negligible, as is the case in molten carbonate fuel cells. More detailed studies concerning the stability problem of this material system, including the chemical stability, evaporation loss as well as corrosion effect to other components, are in progress and will be presented in our next paper.

Such high current density output arose from the high conductivity of the electrolyte, since the electrolyte is as thick as 0.25 mm, and good catalytic activity of both electrodes. From the I–V characteristics, the internal resistance of the whole single cell could be derived, and then the approximate dc conductivity of the electrolyte could be obtained by eliminating the effect of both electrodes. Fig. 6 shows the temperature dependence of the conductivity of the composite electrolyte, which was deduced from the I–V characteristics. The ac conductivities of pure GDC and YSZ tablets sintered at 1500 °C for 5 h were also included as a comparison. It is obvious that the conductivity of the composite electrolyte is about 3−10 times higher than that of pure GDC, and more than two orders of magnitude higher
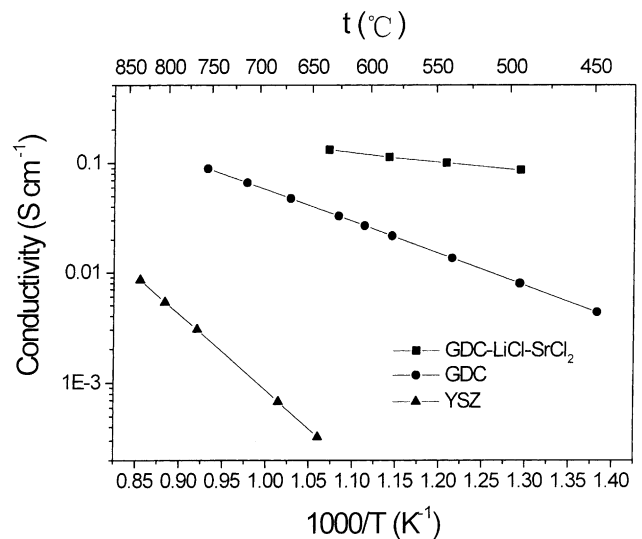

Fig. 5. Typical I–V and I–P characteristics for fuel cells using GDC–LiCl–SrCl$_2$ composite electrolyte at 550, 590 and 625 °C, respectively.

Fig. 6. Temperature dependence of the dc conductivity of GDC–LiCl–SrCl$_2$ composite electrolyte under fuel cell environment. The ac conductivity of pure GDC and YSZ electrolyte was also drawn for comparison.

than that of YSZ at the intermediate temperature range. For example, it reaches 0.13 S cm^{-1} at $650\,^\circ$C, compared to 0.033 S cm^{-1} for pure GDC and 3.2×10^{-4} S cm^{-1} for YSZ at the same temperature. This indicates that the salt plays an essential role in the electrical conduction.

The composite electrolyte contains one solid phase, GDC, and one molten phase LiCl–SrCl$_2$. In the molten phase, the cations, Li$^+$ and Sr^{2+}, and the anion, Cl$^-$, are all mobile. However, when the fuel cell is discharging steadily, all these ions are blocked by the electrodes and do not have any contribution to the current output. Thus, the charge carriers that have contribution to the current output include O^{2-}, H$^+$, and electron (or electron hole). The fact that the OCV is about 0.85 V indicates the transference number of electron (or electron hole) will be less than 0.3, according to the following equation:

$$OCV = (1 - t_e)emf \tag{1}$$

where emf is the theoretical electromotive force (1.1–1.2 V in this case) and t_e is the transference number of electron (or electron hole). It should also be noted that other factors, such as the not fully densified electrolyte and not perfectly reversible electrodes, are also responsible for the lowered OCV. This means that the transference number of electron or (electron hole) may be far less than the value calculated from Eq. (1), i.e. 0.3. Therefore, the conductivity data shown in Fig. 6 mainly reflected the oxygen ion or proton conductivity of the composite electrolyte. The greatly improved ionic conductivity after adding certain amount of LiCl–SrCl$_2$ salts indicated that the LiCl–SrCl$_2$ salts and the interfaces between the salts and GDC exhibit distinct proton or oxygen ion conduction.

In chlorides, NaCl was first found to have both proton and oxygen ion conduction [12]. For the GDC–LiCl–SrCl$_2$ composite electrolyte, the molten LiCl–SrCl$_2$ salts should also provide an effective conducting path for protons and/or oxygen ions. First, protons or oxygen ions are doped into the molten salt, which contains no oxygen or hydrogen element, then the protons or oxygen ions diffuse through the salt under the drive of the electrochemical potential difference between the anode side and cathode side of the electrolyte. The fast transportation of proton or oxygen ion in the molten chloride salts is a new phenomenon, and the detailed conduction mechanism needs further investigation.

In our experiment, we have observed water formation on both sides of the cell, but we still could not determine the transference number of proton or oxygen ion since gas crossover could not be excluded. Therefore, more precise experiment is needed to accurately measure the water amount on both sides.

It was early reported that the addition of a second phase (such as Al$_2$O$_3$, CeO$_2$, SiO$_2$) into the salt phase not only greatly improves the mechanical strength but also enhances the conductivity of the materials [19–22]. This conductivity enhancement is assumed to be due to the formation of a highly conductive region at the interfaces between the salt

and oxide. In the GDC–LiCl–SrCl$_2$ composite, there may exist the same effect, namely "composite effect". The interface between the GDC particles and salt phase may provide another fast ionic transport way.

In the composite electrolyte, the oxide phase, GDC, a well-known good oxygen ion conductor at intermediate temperature range, provides not only a fast oxygen ionic conduction path but also a framework for the molten phase. The combination of GDC and chloride salts successfully further improved the electrical property. Compared with pure GDC electrolyte, this composite electrolyte has many advantages, e.g. (1) it has much higher electrical conductivity than GDC at intermediate temperature range so that it can further reduce the operating temperature of the fuel cell; (2) it decreases the materials cost because the salt is much cheaper than the rare-earth-doped ceria; (3) it does not need so high sintering temperature as pure GDC in the preparation procedure, which usually needs 1400–$1500\,^\circ$C to be sintered, so fabrication costs are low. These advantages, as well as the above results, make this composite electrolyte a competitive candidate for low-cost ITFCs.

4. Conclusions

A new type of oxide-salt composite electrolyte, GDC–LiCl–SrCl$_2$, was developed and used as the electrolyte for intermediate temperature fuel cells. This composite electrolyte exhibited much higher electrical conductivity than pure GDC electrolyte, so that the composition of GDC and chloride salts successfully improved the current and power density output at intermediate temperature range. Higher OCV and hence higher power density output could be expected after applying better preparation technique. The successful utilization of such kind of composite electrolyte greatly extended our searching field for finding appropriate electrolytes for ITFCs. Moreover, to evaluate the practical applicability of fuel cells based on this kind of composite electrolyte, more work concerning its long-term stability is needed.

Acknowledgements

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