Intermediate temperature fuel cells with electrolytes based on oxyacid salts

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Abstract

Electrolyte materials based on oxyacid salts are a new type of solid ionic conducting system where both cations and protons are mobile. These materials have a face-centred cubic structure. Two different proton coordination states and conduction mechanisms have been recognized in this system. The proton conduction has been used for intermediate temperature fuel cells (ITFC). ITFCs using materials based on nitrate salts as electrolytes are successful, the best fuel cell performance is a current density of 300 mA/cm^2 at 0.75 V. There are still some technical problems to be solved, such as the coexistence of electrode and electrolyte materials, etc., in these fuel cells, and an improvement of the electrode materials is needed for a better performance of the practical fuel cells.

Keywords: Fuel cells; Intermediate temperature; Oxyacid salts; Salt–alumina ceramic composite materials

1. Introduction

Nowadays new power sources are urgently needed. Among many new efforts, solid-state fuel cells are very promising. Conventional high temperature (about 1000 °C) solid-state fuel cells such as the solid oxide fuel cell (SOFC) are beginning to become commercialized today [1]. However, commercialization still has a long way to go because of inherent limits, e.g., special high temperature requirements (about 1000 °C) resulting in high costs. Therefore, it is from some points of view preferable to operate solid-state fuel cells at intermediate temperature (ITFC), e.g., 400 to 600 °C. Fuel cells have a key part, the solid electrolyte in which protons, oxide ions or other ionics species, e.g. NH$_4^+$ or OH$^-$ may be transported. There have been two routes to develop intermediate temperature fuel cells, using either oxide conductors or proton conductors; (see, e.g. the very good review paper on intermediate temperature ionic and protonic conducting oxides by Steele [2]). It has been found that some oxide perovskites (ABO$_3$), e.g. BaTh$_{0.9}$Gd$_{0.1}$O$_{2.95}$, and oxide brownmillerites (A$_2$B$_2$O$_5$), e.g. Sr$_2$Gd$_2$O$_5$, have excellent H$^+$ or OH$^-$ and O^{2-} conductivities in the intermediate temperature range [3–6]. These oxide materials have been successfully demonstrated in ITFCs [3–5]. In parallel with this, proton-conducting oxyacid salts and related composite materials have also recently been developed and used as electrolyte materials for ITFCs [7–12]. Compared with other intermediate temperature oxides, materials based on oxyacid salts may have advantages regarding cost, ease of preparation, and temperature range, etc. ITFC-using materials based on nitrate salts as electrolytes have shown the best fuel cell performance, such as a current density of 300 mA/cm^2 under a cell voltage of 0.75 V. These fuel cells are, therefore, a very promising fuel cell system at intermediate temperatures.

2. Experiments

Electrolyte materials based on oxyacid salts, such as Li$_2$SO$_4$–Al$_2$O$_3$ and RbNO$_3$–Al$_2$O$_3$ were prepared using the solution–gel process as described earlier [13,14]. RbNO$_3$ (p.a., Merck, Germany) and Al(NO$_3$)$_3 \cdot$9H$_2$O (p.a., Merck, Germany) were dissolved in deionized water and sample precursors were recrystallized from the solution with various compositions. The precursors were sintered at 600 °C for 12 h. The sintered products were ground, pressed as a tablet and heated again at 600 °C for 12 h. The final products are used as samples.

Crystal structure and phase transitions were analysed using a Philips power X-ray diffractometer (XRD) and a Rigaku differential thermal analysis (DTA) equipment. Infrared (IR) analyses were performed using a Perkin-

Elmer, 580 B spectrophotometer. IR samples were prepared using the standard KBr method to mix 100 mg sample to 300 mg KBr. IR measurements were carried out for hydrated and deuterated samples as well as for samples used as electrolytes in fuel cells.

The fuel cell was constructed by pressing electrode and electrolyte powders, sandwiched layer by layer, with the cell configuration:

$(H_2$ or town gas) anode/

oxyacid salt based electrolyte/cathode(air)

where the fuel was commercial pure hydrogen (99.9995% pure AGA Gas, Sundbyberg) or a hydrogen-rich (65% H_2) town gas; the oxidant gas was dried air. In this cell, the anode was made using Rancy nickel, 50/50 (KEBO, Stockholm), Ni–NiO, or platinum paste (Leitplatin 308A, Hanau), and the cathode using perovskite oxide $La_{0.6}Sr_{0.4}MnO_3$, NiO–AgO, carbon or silver paste (Leitsilber 200, Hanau). Thicknesses are about 0.1 mm for the electrode layers and about 1–2 mm for the electrolyte. Fuel cells were tablets, 13 mm in diameter, and about 0.60 cm^2 of the cell area was exposed to gas. The fuel cell device used for tests is shown in Fig. 1. The fuel cell was also constructed with different cell sizes and tested in series. Furthermore, to improve fuel cell performance we also used composite electrodes, i.e. mix electrolyte, carbon and electrode materials in a 1:1:1 volume ratio to make electrodes.

The conductivity of the electrolytes can be measured using either I–V curves measured from fuel cells or complex impedance spectra for raw samples in air obtained from a computerized LCR meter. The former is referred to as d.c. conductivity and the latter as a.c. conductivity. Fuel cells were measured using a computerized KEITHLEY 617 programmable electrometer, a Philips PM 2513 digital multimeter, and a Cropico resistance box (0.02% sensitivity). I–V characteristics of fuel cells were recorded under various loads.
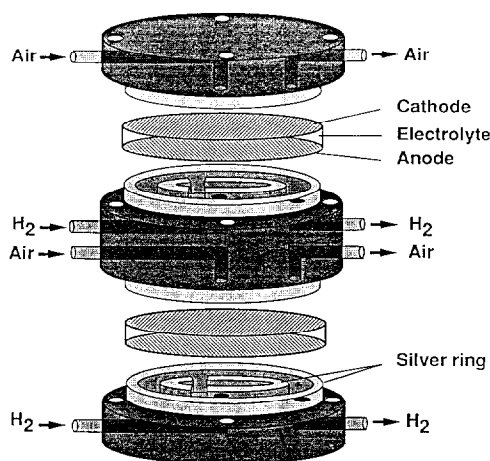
3. Results and discussion

3.1. Structure and electrical properties for electrolytes based on oxyacid salts

Sample precursors contain oxyacid salt, i.e. sulfate or nitrate and $Al(NO_3)_3$ before the high temperature sintering. After sintering $Al(NO_3)_3$ component in precursors is transferred to Al_2O_3. The other sulfates and nitrates are very stable and remains in their phases. No other intermediate phases or solid solutions between oxyacid salt and alumina are detected in the system. The sintered products from oxyacid salt–$Al(NO_3)_3$ precursors are thus salt–alumina ceramic composite materials. The ceramic phase is responsible for the good mechanical strength of these composites.

The structure of these oxyacid salts-based materials is determined by the oxyacid salt phase, and alumina forms an amorphous background. Li_2SO_4 has a first-order phase transition from low temperature (LT) to high-temperature (HT) phase at about 577 °C [15]. The HT phase for Li_2SO_4 is a face-centred cubic rotor phase which has a very high Li^+-cationic conductivity in the order of 1 S/cm at 600 °C. $RbNO_3$ has also a face-centred cubic structure which is stabilized at room temperature by using heat treatment [16]. The structures for these oxyacid salts is schematically given in Fig. 2, where corner- and face-centred sites are occupied by oxyacid groups, such as SO_4, NO_3 and also including PO_4 [10] for sulfates, nitrates, phosphates and composite materials based on these salts. A high proton conductivity of the order of 10^{-2} to 10^{-1} S/cm has been discovered in the HT cubic phase of Li_2SO_4, this value is thus about one to two orders of magnitude lower than that of the cationic conductivity [8]. However, in cubic $RbNO_3$ phase, proton conduction is unlikely to
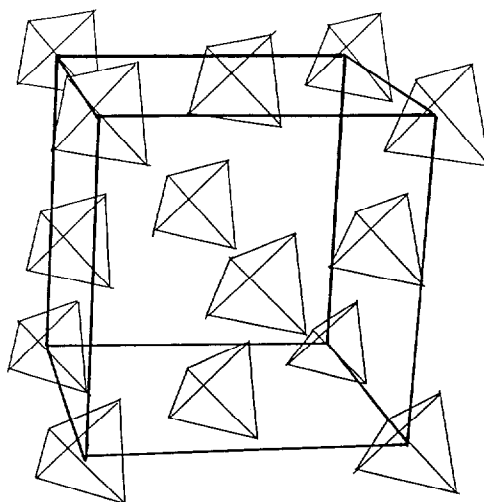

Fig. 1. Test fuel cell setup for two single cells in series.

Fig. 2. Schematic crystal structure of the face-centred cubic oxyacid salts and related composite materials, where face-centred cubic Li_2SO_4 is taken as an example. The tetrahedral here represents SO_4 group.

exist. IR studies reveal the difference between these two materials with the same structure. In Li_2SO_4, there is the proton-coordination bonding, i.e. $H-SO_4$ has been observed in IR spectra for the used fuel cell electrolyte or hydrogen-treated samples, while no such bonding is observed for $RbNO_3$ due to existence of the strong bonding between Rb and NO_3 [16,17]. It becomes possible for the $RbNO_3-Al_2O_3$ composite system, where the strong $Rb-NO_3$ bonding may be broken due to the presence of the second Al_2O_3 phase, which provides coordination sites for protons. Protons then stay at the interface between $RbNO_3$ and Al_2O_3 phases, some bridge ligand bonding between these two phases is formed by the proton coordination, see the configuration (c) of Fig. 3.

Therefore, there are two different coordination states for protons in the $Li_2SO_4-Al_2O_3$ and $RbNO_3-Al_2O_3$ composite electrolytes, which results in two different proton-conduction mechanisms. In the former system, protons directly coordinated with SO_4 group to form a strong $H-SO_4$ bonding, which causes a bulk proton-conduction process by the aid of the paddle wheel mechanism [18,19]. While in the latter, protons at the interface loosely coordinate with both $RbNO_3$ and Al_2O_3, resulting in an interfacial proton-conduction mechanism. The proton-coordination and conduction situation can be presented schematically by Fig. 3. In these materials highly mobile protons are present in very low concentrations resulting in unusually high

proton conductivity. It is thus very important to study the transport mechanism for these dissolved protons.

3.2. Fuel cell performances

Fig. 4 shows $I-V$ characteristics for the fuel cells using various nitrate salt–ceramic composite electrolytes at 400 °C. Among these fuel cells, the $RbNO_3-Al_2O_3$ electrolyte shows the best performance. Therefore, we focus on this electrolyte system. Fig. 5 shows the $I-V$ curves of a fuel cell using the $Li_2SO_4-Al_2O_3$ electrolyte at various temperatures. Compared with the nitrate composites, fuel cells with sulfate composite electrolytes have more technical difficulties.

There is a critical temperature (T_c) observed for fuel cells with nitrate composites as electrolytes. At T_c the fuel cell performance decreases with further increasing temperature. T_c is depending on the used electrode materials. For example, using Pt/Ag and Ni/Ag electrode

Fig. 4. $I-V$ characteristics of fuel cells using various materials based on nitrates as electrolytes at 400 °C. Curves (a), (b), (c), (d), and (e) are for $LiNO_3-Al_2O_3$, $NaNO_3-Al_2O_3$, $KNO_3-Al_2O_3$, $RbNO_3-Al_2O_3$ and $CsNO_3-Al_2O_3$ composite electrolytes, respectively.
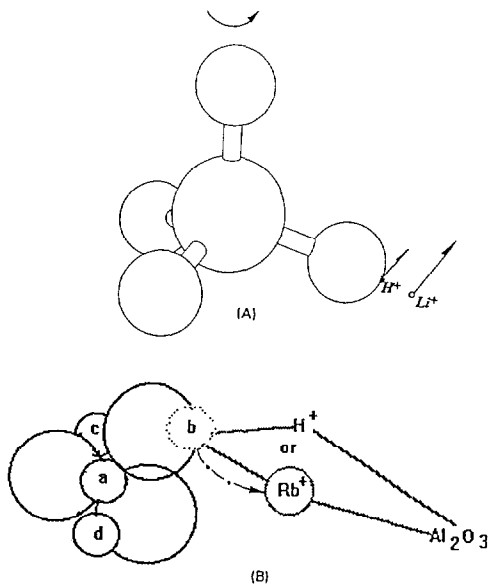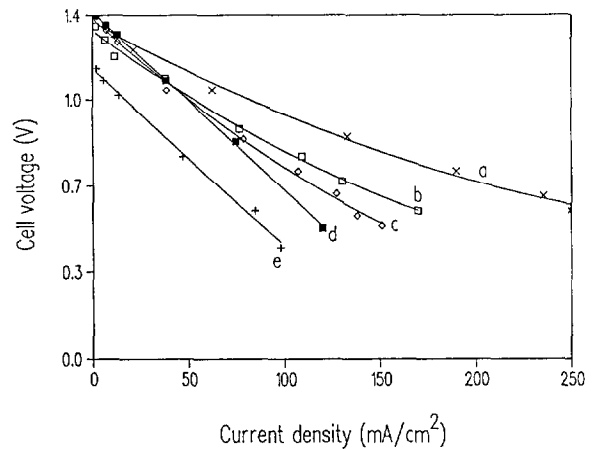

Fig. 3. Configuration for cations and protons coordinations. (A) Sulfates and related composite materials where fast rotation of sulfate group strongly 'push' cations and protons motion; (B) nitrates, where a, b, c and d represent four non-equivalent cation sites around the nitrate ion; for the $RbNO_3-Al_2O_3$ system the coordination bonding between the cation, e.g., cation b, and nitrate ion may be broken, which provides a coordination site for the proton. Thus, both Rb^+ cations and protons may stay at the interface between two phases, as shown here.
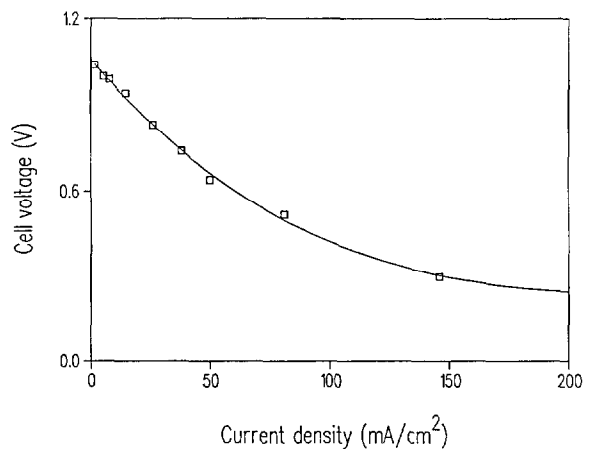

Fig. 5. $I-V$ characteristics of fuel cells using Li_2SO_4-based material as the electrolyte at about 600 °C.

pair, T_c is 430 and 360 °C, respectively. But for the Ni/perovskite oxide pair, T_c is about 500 °C. After the fuel cell operation, we found that there is a black layer between the interface of Ag/electrolyte due to the reaction between silver and electrolyte. This black layer has very poor conductivity and therefore causes a high cell resistance which reduces the cell performance. Fig. 6 shows the I–V characteristics of the RbNO$_3$–Al$_2$O$_3$ fuel cells obtained using different electrodes at temperatures below T_c. In Fig. 6, the fuel cell with the Ni–NiO/NiO–AgO electrode pair shows the best cell performance. For instance, a current density of 200 mA/cm^2 under the cell voltage of 0.75 V is obtained at 400 °C. Such a good cell performance is caused by the excellent electronic and ionic conduction in this electrode pair. On the other hand, the fuel cell using perovskite oxides as cathodes can avoid partially side reaction at the interface of electrode/electrolyte due to the good chemical stability of the oxide. Therefore, these fuel cells have high T_c, 500 °C. After a further increase in temperature, there may be some kind of decomposition of electrolytes, and the performances of fuel cells also decrease. Since the electrical properties of perovskite oxides used here are very poor in the temperature region from 400 to 600 °C, these fuel cells do not have as good performance as that when other electrode pairs under T_c are used. For instance, only 80 mA/cm^2 current density at 0.75 V is obtained when the Ni/perovskite oxide electrode pair is used at 500 °C. Furthermore, to get good mixed conducting properties for electrons and ions in electrodes, we also constructed fuel cells using composite electrodes. A simple way to prepare composite electrodes which have good electrical properties for both electrons and ions is by using a mixture of electrode and electrolyte materials. The former has good electronic conduction and the latter good ionic conduction. The fuel cells
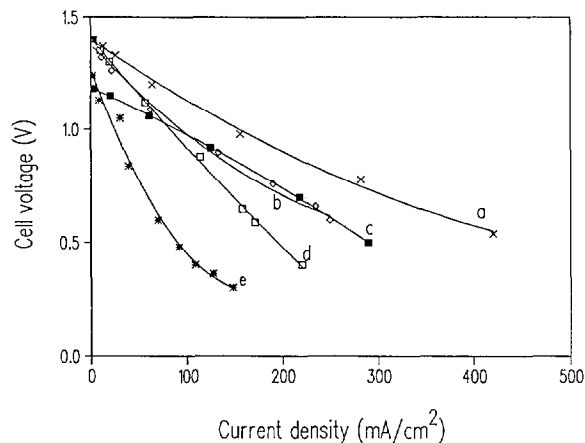
using composite electrode show better performance indeed than those using only pure electrode materials. A typical example of the RbNO$_3$–Al$_2$O$_3$ fuel cells using the Ni–NiO/NiO–AgO pair with composite electrode layers is shown in the curve (a) of Fig. 6, where the current density is as high as 300 mA/cm^2 at 0.75 V. There are different mobile species, such as Rb$^+$, H$^+$, etc., in these electrolyte materials, but only H$^+$ is a non-blocked mobile species and others are blocked in the fuel cell process. The blocked mobile species may have side effects on non-blocked mobile species. One example of these side effects is that there is an unusual character in these studied fuel cells, i.e. a high open-circuit voltage (OCV) value from 1.4 to 1.5 V. This can be explained by the effect of blocked mobile species Rb$^+$ cations to form an ionic concentration potential in the electrolyte [20]. After a certain time to operate the fuel cells, the OCV value then tends to the normal value due to a redistribution of blocked ions in the electrolyte.

I–V characteristics are also measured for fuel cells with 9, 13, 18 and 24 mm in diameters, respectively. It has been observed that the current obtained from these fuel cells are not proportional to cell areas. The bigger the cell area, the more deviation there is from the proportional relationship. This deviation is caused by the poor current collection. This suggests that special electrodes of current collector are required for fuel cells with big areas. In addition, the I–V characteristics are also measured for two single cells in series. This double-cell group shows a successful performance, where OCV, 2.2 V of the designed value, and good I–V characteristics are obtained. These results of the cell group have significant importance to the practical power source.

4. Conclusions

Oxyacid salts based materials are salt–alumina composites, where both cations and protons are mobile. The structure of these oxyacid salt-based materials is determined by the salt phase. High proton conduction takes place in these materials with a face-centred structure. There are two different proton-coordination states and conduction mechanisms in these materials observed which represents typical proton conduction and coordination in oxyacid salts and related composite materials. In the studied fuel cell system the blocked mobile Rb$^+$ species may cause a higher OCV of the fuel cells. The RbNO$_3$–Al$_2$O$_3$ ITSFCs have shown the best fuel cell performance, e.g. 300 mA/cm^2 at 0.75 V. A test of two cells in series shows a good cell performance which is important for the application in a practical power source system. There are still problems in these fuel cell systems such as the existence of a critical

Fig. 6. I–V characteristics of fuel cells using various electrode materials for temperatures below T_c: curves are for (a) the composite electrodes, (b) Ni–NiO/NiO–AgO, (c) Pt/Ag, (d) Ni/Ag and (e) Ni/perovskite oxide, respectively.

temperature, T_c, which is caused by either the reaction between the electrode and electrolyte materials, or some kind of decomposition of the electrolytes at high temperatures. To solve this problem, it is urgent to develop new electrode materials which have good electrical properties and chemical stability in ITSFCs.

Acknowledgement

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