NOVEL PROTON CONDUCTING CERAMICS FOR
SOLID STATE FUEL CELLS

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ABSTRACT

Novel proton conducting ceramics based on oxyacid salts, e.g. Li$_2$SO$_4$, K$_3$PO$_4$ and RbNO$_3$ have been prepared. High proton conduction normally appears in the cubic symmetry structures of these ceramics. The structural and electrical properties depend upon the ceramic composition and sintering process. These oxyacid salt ceramics have a proton conductivity of the order of $10^{-2}$ S/cm at 600°C, the highest value of $10^{-1}$ S/cm at 600 °C was obtained for Li$_2$SO$_4$-Al$_2$O$_3$ ceramics. The oxyacid salt ceramics have been used in intermediate temperature (500 °C - 650 °C) solid state fuel cells, but they can also be used for high temperature fuel cells. The performance of the oxyacid salt ceramics fuel cell was mainly limited by the electrode materials, not by the electrolyte.

1. INTRODUCTION

High temperature proton conduction in oxyacid salts has been studied by our group during recent years [1-4]. These oxyacid salts involve a very wide range of compounds, e.g. sulphates, phosphates, nitrates and carbonates etc. and related multi-component systems. The highest proton conductivity of these oxyacid salts is about $10^{-2}$ S/cm at 600 °C and fuel cells using oxyacid salts as electrolyte have been successfully demonstrated [1-4]. Although the oxyacid salts have high proton conductivity and may be used in the future for applications such as intermediate and high temperature solid state fuel cells, there are still some practical aspects to be considered, such as mechanical strength, gas permeation, chemical and electrochemical stability, film preparation etc.. To improve some of the properties of these materials, ceramics based on oxyacid salts have been developed.
2. EXPERIMENTAL

The oxyacid salts used in this work are Li$_2$SO$_4$·H$_2$O (A.R., Merck, Germany), K$_3$PO$_4$·nH$_2$O (A.R., Mallinkrodt, USA) and RbNO$_3$ (99% pure, Merck, Germany). The Al(OH)$_3$ gel was prepared from solutions of Al$_2$(SO$_4$)$_3$·18H$_2$O (A.R., Mallinckrodt, USA) and NaOH (98% pure, EKA, Sweden). 0.1 M solution of the oxyacid salt in deionized water was titrated into 0.1M Al(OH)$_3$ gel with a rate of 1-2 ml/min for various M(M = Li, K, Rb)/Al ratios. The titration was accompanied by a stirring and heating process. The ceramics were formed in two steps; First the ceramic precursors were prepared by the gel solution process and then the ceramics were prepared by sintering the precursors at 800 to 900 °C for more than 10 hours depending on the composition. Various sintering processes at lower temperatures (500 to 800 °C) were also studied in some cases. The samples were calcined in a platinum crucible. The structural properties of the ceramics were studied by X-ray diffraction (XRD), using a Philips diffractometer with Ni filtered, Cu Ka radiation. The electrical properties were measured by a computer controlled complex impedance analyser (Hewlett-Packard HP4274) and by hydrogen concentration cells (HCC) [2]. The proton conductivity of the samples can be also estimated from the fuel cell measurements. Platinum paste (Leitplatin 308A, Demetron, Hanau, Germany) was used as electrode materials of both A.C. and D.C. electrical measurements. Solid state fuel cells were constructed using oxyacid salt ceramics as electrolytes, perovskite oxide La$_{0.85}$Sr$_{0.15}$MnO$_3$ (provided by Risø National Lab., Denmark) and Raney-nickel (KEBO AB, Stockholm) as electrode materials. Both perovskite oxide and nickel electrode materials were mixed with active carbon, and electrolyte material in a certain component ratio to make composite electrodes for the fuel cells. Air and commercial hydrogen gas were used for oxidant and fuel of the fuel cells. The electrolyte pellets with composite electrodes of perovskite oxide and nickel were first preheated in air at 500 to 800 °C for 5 - 20 hours depending on the electrolyte materials, then heated again in hydrogen at 600 °C for severeral hours. After this treatment the nickel electrode became partially oxidated to form a Ni-NiO electrode. The pellets for both electrical measurements and fuel cells had a thickness of 1-2 mm and an area, 9 mm in diameter, was exposed to the gas. The polarization study of the fuel cell was performed using an additional reference electrode which was made of a fine platinum wire (diameter 0.1mm) in the middle of the electrolyte. The current-voltage(I-V) characteristics of fuel cells were measured using a computerized Keithley 617 Programmable Electrometer, a Schlumberger - Solartron 7040, and a Cropico Resistance Box (0.02% sensitivity). The DTA measurements were performed using a Rigaku thermal analysis equipment.
3. STUDIES ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF THE ELECTROLYTES

3.1 Li$_2$SO$_4$ - Al$_2$O$_3$ Ceramics

Li$_2$SO$_4$, the subject of long-standing scientific interest, has two phases at normal pressure. The low temperature phase, $\beta$-Li$_2$SO$_4$, has a monoclinic structure, space group P2$_1$/a [5]. At 577 °C, a first order phase transition takes place, involving a much higher transition enthalpy than that of the melting [6]. The structure of the high temperature phase is face centered cubic, space group Fm3m [7]. This phase transition temperature can be lowered by doping with other salts [8]. XRD and DTA analyses show that in the Li$_2$SO$_4$-Al$_2$O$_3$ ceramics prepared using the gel solution process the Li$_2$SO$_4$ phases and an amorphous Al$_2$O$_3$ background dominate but there may be more intermediate phases in the system [9]. The determined conductivities from complex impedance analysis ($\sigma_{ac}$), hydrogen concentration cells ($\sigma_{dc}$) or fuel cells ($\sigma_{fc}$) for Li$_2$SO$_4$-Al$_2$O$_3$ ceramics containing approximately 45 mol% Al$_2$O$_3$ are shown as a function of temperature in Figure 1. The phase transition temperature (about 450 °C) is much lower than that of Li$_2$SO$_4$ (577°C). The difference in conductivity between high and low temperature phases is also less than that of Li$_2$SO$_4$. For the high temperature phase of the Li$_2$SO$_4$-Al$_2$O$_3$ ceramics, $\sigma_{dc}$ is lower than $\sigma_{ac}$, the total ionic conductivity, including contributions from both cations and protons. For the low temperature phase (T < 450 °C) this difference is less. Anyway, the D.C. conductivity for the high temperature phase calculated from the fuel cell measurements, $\sigma_{fc}$, is higher than $\sigma_{dc}$ and closer to $\sigma_{ac}$ (see Fig. 1). This is also true for other oxyacid salt ceramics. The difference between $\sigma_{dc}$ and $\sigma_{fc}$ is caused by the different measuring methods (see section 4). At 480 °C the total ionic conductivity of Li$_2$SO$_4$-Al$_2$O$_3$ ceramics can be enhanced three to four orders of magnitude compared to that of Li$_2$SO$_4$, e.g. for the ceramics containing ~45 mol% Al$_2$O$_3$, $\sigma_{ac} = 10^{-1}$ S/cm.

3.2 K$_3$PO$_4$ - Al$_2$O$_3$ Ceramics

K$_3$PO$_4$ has not attracted much scientific interest as a solid electrolyte. A relatively high ionic conductivity can, however, be obtained for the cubic K$_3$PO$_4$ polymorph [3]. For K$_3$PO$_4$ a low temperature $\alpha$- phase and for temperatures above 550°C a cubic form have been reported [10]. This cubic phase may be stabilized to room temperature [11]. However, in the K$_3$PO$_4$-Al$_2$O$_3$ ceramics the structure depends on the composition and sintering process. The cubic K$_3$PO$_4$ phase was sometimes formed by sintering the K$_3$PO$_4$-Al(OH)$_3$ precursor in a mole ratio of about 1:1 at about 530 °C in a closed container for one week. Using a high temperature (T > 800 °C)
sintering process in air both a transparent glassy material and mixed glass-ceramics can be produced using different precursor compositions and quenching process. When the precursor containing $\text{K}_3\text{PO}_4 : \text{Al(OH)}_3$ in a mole ratio at about 1:1 was heat-treated at 830 °C, the sample was partially molten. The molten part of the sample can be quenched to room temperature to form the pure glassy material. On the other hand, the glass-ceramic material was obtained easily for the partially molten melt sample or without quenching in most cases. Therefore, studies were mainly performed for the glass-ceramic samples. The XRD results of these materials are shown in Figure 2 and 3. One can also find from Fig. 2 that the glass-ceramics contains the cubic $\text{K}_3\text{PO}_4$ as the main crystalline phase. A lattice parameter of $8.860 \pm 0.005 \text{ Å}$ was obtained for the face-centered cubic structure using least squares fitting. Figure 4a shows Arrhenius curves of a.c. and d.c. conductivities for ceramics containing about 25 mol% $\text{Al}_2\text{O}_3$. In Fig. 4a the values for $\sigma_{ac}$ and $\sigma_{dc}$ are of the same order for the $\text{K}_3\text{PO}_4-\text{Al}_2\text{O}_3$ ceramics. This means that proton conduction is the main contribution to the conductivity of the sample. In addition, if a sample is kept in the hydrogen atmosphere of the concentration cell, $\sigma_{dc}$ gets even higher than the measured $\sigma_{ac}$ in air (see Fig.4a) because of an increased concentration of protons. Similar results have been observed for pure $\text{K}_3\text{PO}_4$ that has been kept in a hydrogen atmosphere [3]. It can be also seen from Fig. 4a that there is a first order phase transition at about 550 °C which causes a conductivity increase of about two orders of magnitude. It seems to be identical to the transition to the high temperature cubic phase of $\text{K}_3\text{PO}_4$.

3.3. $\text{RbNO}_3 - \text{Al}_2\text{O}_3$ Ceramics

$\text{RbNO}_3$ has a structure that is isomorphous with $\text{CsNO}_3$ at room temperature and three different phases have been reported at higher temperatures [12-13]. As the temperature increases, the structure changes from trigonal to CsCl, rhombohedral and finally to NaCl structure [13,14]. In $\text{RbNO}_3-\text{Al}_2\text{O}_3$ ceramics prepared by the gel-solution technique a cubic phase can be identified in the XRD pattern at room temperature, mixed with traces of other phases which are difficult to distinguish due to the low intensity of the diffraction peaks, see Figure 3. A cubic lattice parameter of $7.860 \pm 0.005 \text{ Å}$ was found using a least squares fitting program. Figure 4b shows the Arrhenius curves of $\sigma_{ac}$ and $\sigma_{dc}$ for $\text{RbNO}_3-\text{Al}_2\text{O}_3$ ceramics with approximately 60 mol% $\text{Al}_2\text{O}_3$. Also in this case, all the measured conductivity values are close, suggesting that protons dominate the conductivity in this system.
3.4. Studies on the Gas Concentration Cells

Two kinds of gas concentration cells were investigated for the oxyacid salt ceramics.

\[ \text{O}_2 / \text{Pt} / \text{Oxyacid salt ceramics} / \text{Pt} / 2\% \text{O}_2 \text{ in Ar} \]
\[ \text{H}_2 / \text{Pt} / \text{Oxyacid salt ceramics} / \text{Pt} / 5\% \text{H}_2 \text{ in Ar} \]

The gas concentration cell measurements covered a wide temperature range. Usually, almost no emf was observed for oxygen concentration cells in the studied temperature range. In some case about 20 to 30 mV was measured for \( \text{RbNO}_3\text{-Al}_2\text{O}_3 \) ceramics in the oxygen concentration cell at temperatures above 600 °C. On the contrary, the hydrogen concentration cells were always responding sensitively for different partial pressures of hydrogen gas. These results suggest that the oxyacid salt ceramics are mainly proton-type conductors, not oxygen conductors. These ceramic materials thus have similar proton conduction properties as the oxyacid salts [1-4].

3.5. Other Systems

The pseudo-binary system \( \text{K}_3\text{PO}_4\text{-RbNO}_3 \) was also studied. A mixture of \( \text{K}_3\text{PO}_4\text{-RbNO}_3 \) in a mole ratio of 60 : 40, which was calcined at about 530 °C for one week, shows a two-phase mixture of and a phase which might be indexed as cubic (shown in Fig. 2c) with a lattice parameter of 7.405 ± 0.005 Å. For the high

Table I The electrical properties for various oxyacid salt ceramic systems

| Sample                  | \( \sigma_{\text{a.c.}} \) (S/cm) | \( \sigma_{\text{d.c.}} \) (S/cm) | Temperature (°C) |
|-------------------------|----------------------------------|----------------------------------|------------------|
| \( \text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3 \) | 0.1 - 1.0                        | 10\(^{-2}\) - 0.1                | \( T > -480 \) |
| \( \text{K}_3\text{PO}_4\text{-Al}_2\text{O}_3 \) | \( 10^{-3} - 10^{-2} \)          | \( 10^{-3} - 10^{-2} \)          | \( T > -550 \) |
| \( \text{RbNO}_3\text{-Al}_2\text{O}_3 \)     | \( 10^{-3} - 10^{-2} \)          | \( 10^{-3} - 10^{-2} \)          | \( T > -400 \) |
| \( \text{K}_3\text{PO}_4\text{-RbNO}_3 \)     | \( 10^{-3} - 10^{-2} \)          | \( 10^{-3} - 10^{-2} \)          | \( T > -400 \) |
| \( \text{K}_3\text{PO}_4\text{-RbNO}_3\text{-Al}_2\text{O}_3 \) | \( 10^{-3} - 10^{-2} \)          | \( 10^{-3} - 10^{-2} \)          | \( T > -350 \) |
| \( \text{Li}_2\text{SO}_4\text{-LiOH-Al}_2\text{O}_3 \) | 0.1 - 1.0                        | 10\(^{-2}\) - 0.1                | \( T > 450 \) |
| \( \text{Li}_2\text{SO}_4\text{-ZrO}_2 \)     | 0.1 - 1.0                        | 10\(^{-2}\) - 0.1                | \( T > 450 \) |
| \( \text{K}_3\text{PO}_4\text{-SiO}_2 \)      | \( 10^{-3} - 10^{-2} \)          | \( 10^{-3} - 10^{-2} \)          | \( T > 510 \) |
| \( \text{K}_3\text{PO}_4\text{-ZrO}_2 \)      | 10\(^{-2}\)                      | 10\(^{-2}\) - 10\(^{-2}\)        | \( T > 500 \) |
temperature (800 - 900 °C) sintered K₃PO₄-RbNO₃ sample, the diffractogram is dominated by a strong amorphous background. Both types of samples have similar conductivity. Table I lists the conductivities for various oxyacid salt ceramics systems.

Some three component systems as well as some systems with a different oxide, e.g. ZrO₂, or SiO₂ were also studied. The Li₂SO₄-ZrO₂ ceramic has similar phase transition and electrical properties as the Li₂SO₄-Al₂O₃ ceramics. These results are also included in Table I.

4. STUDIES ON INTERMEDIATE TEMPERATURE SOLID STATE FUEL CELLS

A large number of solid state fuel cells using oxyacid salt ceramics have been investigated. Figures 5 shows typical I-V characteristics of the fuel cells. The best cell performance was achieved by the Li₂SO₄-Al₂O₃ ceramics fuel cell. The short circuit current density of the cell is close to 600 mA/cm² at 600 °C. The study of the cell polarization shows that the cell voltage loss under load is caused mainly by the cathode and anode materials, not by the electrolyte. Figure 6a shows the polarization properties for the cell cathode and anode of the Li₂SO₄-Al₂O₃ ceramics fuel cell. Figure 6b shows the voltage loss for both electrodes given considerations to the correction for ohmic loss of the cell electrolyte. From these Figures one can clearly see that electrode polarization causes about 70% of the total voltage loss for current densities above about 50 mA/cm². This fact shows that the electrode materials is what predominantly limits the cell performance. If the properties of the electrode materials can be improved, a current density of more than 1.0 A/cm² at 600 °C could be reached. The cell resistance (Rₑ) can be divided into the resistance of the electrode (Rₑ) and the electrolyte (Rₒ). Based on the principle of the electrode kinetics and the cell process [15], these resistances of the cells can be calculated. Table II lists the cell parameters using the I-V curves in

| Electrolyte       | OCV (V) | Rₑ (Ω) | Rₒ (Ω) | Rₑ (Ω) | Temperature (°C) |
|-------------------|---------|--------|--------|--------|------------------|
| Li₂SO₄-Al₂O₃      | 1.0-1.1 | 6.5    | 1.2    | 5.3    | 600              |
| K₃PO₄-Al₂O₃       | 1.0-1.1 | 18.5   | 7.8    | 10.7   | 640              |
| RbNO₃-Al₂O₃       | 1.0-1.05| 10.4   | 3.6    | 6.8    | 640              |
| K₃PO₄-RbNO₃      | 1.1-1.15| 22.5   | 9.8    | 12.7   | 650              |
Fig. 5. The I-V characteristics of the fuel cells can be divided into two linear regions, A and B. Region A represents mainly the electrode process, where the cell potential losses are caused by the activation overpotential, e.g. lack of electrocatalysis, sluggish electrochemical reaction and ohmic resistance of the electrode etc.. Region B reflects the electrolyte conduction process, where the linear drop of the cell potential is dominately caused by the ohmic losses in the cell electrolyte. Therefore from the slopes of these regions, one can estimate separately $R_e$ and $R_o$. Based on the calculation of $R_o$, a proton conductivity of $10^{-1}$ S/cm was obtained for Li$_2$SO$_4$-Al$_2$O$_3$ ceramics and $10^{-2}$ to $10^{-1}$ S/cm for K$_3$PO$_3$-Al$_2$O$_3$ and RbNO$_3$-Al$_2$O$_3$ ceramics at 600 °C. The conductivity $\sigma_{dc}$ estimated from fuel cells for various ceramic electrolytes are shown in the corresponding Arrhenius curves (see Figs. 1 and 4). From Table II one can find that the electrode resistance is the main part of the total fuel cell resistance. This is especially pronounced for electrolytes with high ionic conduction, e.g. Li$_2$SO$_4$-Al$_2$O$_3$ ceramics. It is reasonable that there is a difference between $\sigma_{dc}$ and $\sigma_{fc}$ since $\sigma_{dc}$ contains the electrode resistance, while for the measurement of I-V characteristics of fuel cells, it is possible to separate the resistances of the electrode and the electrolyte. In fact, some of the solid state oxyacid salt ceramics fuel cells can be operated at high temperatures, e.g. 600 to 1000 °C. The lower operating temperature of the fuel cells is limited due to the electrochemical reactions and the electrical properties of the electrode materials. For instance, for temperatures below 500 °C, an open circuit voltage of less than 0.5 V was observed for the Li$_2$SO$_4$-Al$_2$O$_3$ ceramics fuel cells. Therefore, to develop electrode materials for the solid oxyacid salt ceramics fuel cells is very important and urgent.

The ceramics based on oxyacid salts are very interesting proton conductors and promising electrolyte materials for intermediate and high temperature solid state fuel cells. Compared to the pure oxyacid salts the ceramic materials have improved properties. These new ceramic materials can thus become an alternative for solid state fuel cells with a lower operating temperature than the traditional high temperature SOFC.

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Figure 1. Temperature dependence of the conductivities of Li$_2$SO$_4$-Al$_2$O$_3$ ceramics.
Figure 2. XRD patterns for various oxyacid salt ceramics, where a), b), c) and d) are for K$_3$PO$_4$-Al$_2$O$_3$ glass, K$_3$PO$_4$-Al$_2$O$_3$ glassy-ceramics, K$_3$PO$_4$-RbNO$_3$ and RbNO$_3$, respectively.

Figure 3. XRD patterns for cubic phases of the oxyacid salt ceramic samples.
Figure 4. Temperature dependence of the conductivities, for (a) K₃PO₄-Al₂O₃; (b) RbNO₃-Al₂O₃.
Figure 5. Current-Voltage characteristics for solid state oxyacid salt fuel cells, for (a) the Li$_2$SO$_4$-Al$_2$O$_3$ ceramic electrolyte fuel cell at various temperatures; (b) the other oxyacid salt ceramic electrolyte fuel cells, where a), b) and c) are for RbNO$_3$-Al$_2$O$_3$, K$_3$PO$_4$-Al$_2$O$_3$, and K$_3$PO$_4$-RbNO$_3$ at 630 °C, respectively.
Figure 6. Polarization curves and voltage loss for the anode and cathode of the Li₂SO₄-Al₂O₃ ceramic electrolyte fuel cell, (a) Polarization curves at different temperatures; (b) Voltage loss curves at 600 °C, where the thicker and thinner curves are before and after the correction for the electrolyte ohmic loss, $V_{ca}$ and $V_{an}$ are the potential values of the cathode and anode, and $IR_{cp}$, $IR_{ap}$ and $IR$ are the voltage loss for the cathode, anode and electrolyte, respectively.