

# New advanced ceramic fuel cell technology using $\text{MF}_x$ ( $\text{M} = \text{Na}, \text{Ca}, \text{Ba}, \text{La}, x = 1-3$ ) based electrolytes

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Received 28 January 1999; received in revised form 23 April 1999; accepted 27 April 1999

## Abstract

The operation of new advanced ceramic-type fuel cells (FCs) using  $\text{MF}_x$  ( $\text{M} = \text{Na}, \text{Ca}, \text{Ba}, \text{La}, x = 1-3$ ) based electrolytes was studied. Various FC construction techniques and electrode materials were investigated. Among them, the  $\text{LiNiO}_2$  anode-supported cell has shown the best performance, 200 mA/cm<sup>2</sup> at 0.4 V can be reached, based on bulk materials. The conductivity and ionic transport properties for the  $\text{MF}_x$ -based electrolytes have also been investigated. During the FC's operation, water was often observed at the cathode, indicating that proton conduction occurs in these electrolyte materials. The experiments indicate an interesting chance for the future development of innovative FC technology. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Fuel cell; Fluoride-based electrolytes; Proton conduction; *I*-*V* characteristics

## 1. Introduction

Intermediate temperature (400–800°C) fuel cells (ITFCs) have been strongly developed in recent years. Ceramic membranes of doped ceria (an  $\text{O}^{2-}$  conductor) and oxyacid salt and salt-oxide composites (SOCs) (mainly  $\text{H}^+$  conductors), e.g.,  $\text{Li}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$ , are being investigated [1–6]. ITFCs are attractive since they combine the advantages of both high and low temperature fuel cells (FCs) such as fast electrode kinetics, fuel flexibility, and low material costs, ordinary materials can be used for the construction of the system. In his review on the world-wide FC efforts and future prospects, Appleby [7] mentioned the attractiveness of SOC materials for FCs [4]. The most successful innovation for SOC FCs consists in the new hydrogen sulphide desulfurization/FC co-generation that has been recently demonstrated using  $\text{Li}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$  electrolytes [8–11]. The co-generation offers a solution to two important issues: removing industrial  $\text{H}_2\text{S}$  emissions, and simultaneously producing electricity or  $\text{H}_2$ .

ITFCs are significant for the development of new marketable FC technology in either transportation or stationary generating plants. The discovery of fluoride-based materi-

als for FC electrolytes, and the performance of the FCs presented in this paper may offer new opportunities for developing advanced FC technology for commercialisation.

## 2. Experimental

### 2.1. Cell and ancillary materials

Materials used for the cell construction are: electrolytes of the type  $\text{MF}_x$  ( $\text{M} = \text{Na}, \text{Ca}, \text{Sr}, \text{Ba}, \text{La}, \text{etc.}, x = 1-3$ ), and alumina (Merck); electrodes of the type  $\text{Co}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and oxides with a layered rock salt structure, such as  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ . The latter were provided by the University of Science and Technology of China (USTC) through the NUTEK (Swedish National Board for Technical Development)–MSTC (Ministry of Science and Technology of China) bilateral co-operative agreement. These layer structured oxides were used for the FC anode and cathode. Perovskite oxides, i.e.,  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$  and  $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_3$  (Seattle Specialty Ceramics, Seattle, WA, USA), platinum (Leitplatin 308A, Hanau, Germany) and silver (Leitsilber 200, Hanau, Germany) pastes were also investigated for the electrodes. Stainless steel was used for the interconnectors and the bi-polar plates. Alumina, a common medium for the second phase mate-

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rial, was used to prepare  $\text{MF}_x$  composites. Both pure fluoride and composite samples used for the measurements were first pressed as pellets and then heat-treated at  $800^\circ\text{C}$  for 6 h in air. The heated samples were directly taken out from the furnace to room temperature, then ground thoroughly for cell construction.

## 2.2. FC construction

### 2.2.1. Composite electrode (anode and cathode) / electrolyte bilayer-supported FCs

(i) A composite anode was made by a mixture of electrolyte (40 vol.%), anode, e.g.,  $\text{LiNiO}_2$  (40 vol.%) and carbon/graphite (20 vol.%) powders. After sintering, the carbon/graphite was removed from the mixture in order to form a porous structure in the anode; (ii) a composite cathode was made by the same procedure using cathode material, e.g.,  $\text{LiCoO}_2$ , instead of  $\text{LiNiO}_2$ . The composite electrode/electrolyte bilayer-supported FCs were constructed first as a bilayer assembly of electrolyte/composite anode, or electrolyte/composite cathode, which was made by directly pressing the electrolyte and composite electrode materials together at pressures of 200 to 300 MPa. The bilayer assembly had the electrolyte layer  $\sim 0.5$  mm in thickness and the electrode layer  $\sim 1.0$  mm in thickness, respectively. After heat-treatment, Ag paste was applied on top of the electrolyte for the electrolyte/composite anode bilayer, and Pt paste applied to the electrolyte/composite cathode bilayer, to complete the construction of the bilayer-supported FCs. The FC was also made by directly pressing the anode, electrolyte and cathode in one step when oxides were used for the electrodes. To avoid the cracking and separation of the FC components (anode, electrolyte and cathode) during heating, both the bilayer and FC assemblies were heat-treated using a program-controlled furnace to carefully adjust the temperature rise and holding time, e.g., for 30 min at  $800^\circ\text{C}$ .

### 2.2.2. Electrolyte-supported cells

The electrolyte disc (thickness  $\sim 1$ – $2$  mm) was pressed directly from the  $\text{MF}_x$  or from composite powders. After sintering, a Pt anode paste and a Ag cathode paste were applied on each surface of the electrolyte disc to obtain a complete FC assembly. This assembly was heat-treated at  $600^\circ\text{C}$  for 30 min.

The FC assemblies made either by the bilayer- or the electrolyte-supported technique were mounted into the FC device with the following configuration: anode ( $\text{H}_2$  chamber)/ $\text{M}_x\text{F}$ -based electrolyte/cathode (air chamber), the cell size normally being 13 mm in diameter and 2.0 mm thick. Other details have been previously reported [5].

## 2.3. Characterisation

Electromotive forces (EMFs) were measured using a Schlumberger Solartron 7150 + digital multimeter or a

Keithley 616 electrometer with an input resistance of  $10^{12}$  or  $10^{14} \Omega$ .  $I$ - $V$  characteristics were determined by using an equipment for measuring current and voltage under variable loads. The temperature of the FC was controlled by a Eurotherm temperature controller and temperature of the sample was measured using a platinum vs. platinum–10% rhodium thermocouple attached close to the sample.

Conductivity of the electrolyte materials was obtained from measurements of the FC  $I$ - $V$  characteristics, subtracting of the influence of the electrodes. The FCs were operated in the intermediate temperature region, 400 to  $800^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Properties of the electrolytes

It is known that the fluorides are anionic  $\text{F}^-$ -conducting materials [12–16]. Study of the intrinsic conductivity for  $\text{F}^-$  ions of these materials is not the purpose of this paper. In order to distinguish their conducting properties for protons or oxide ions, hydrogen–air FCs using fluoride-based materials as the electrolytes were studied. In this case, only  $\text{H}^+$  or  $\text{O}^{2-}$  are non-blocking mobile ionic charge carriers for steady-state FC current output provided by the reversible gas electrodes. Other ions, e.g.,  $\text{F}^-$ , are blocking, and would not contribute to the steady-state current during FC operation. The same situation also occurs in  $\text{Li}_2\text{SO}_4$  or oxyacid salt FCs [3–5,8–11]. To further distinguish the charge species being transported, i.e., protons and oxide ions, hydrogen and oxygen gas concentration cells were also studied, as was done for proton transport in oxyacid salts, e.g.,  $\text{Li}_2\text{SO}_4$  [17,18].

Some fluorides, e.g.,  $\text{MF}_x$  ( $\text{M} = \text{Na}, \text{Ba}, \text{La}, x = 1$ – $3$ ), have relatively high intrinsic defect concentrations and good conductivity, e.g.,  $10^{-2}$  S/cm at  $700^\circ\text{C}$ . Doping and forming composite with  $\text{Al}_2\text{O}_3$ , can, for most fluoride-based electrolytes, result in a lower FC operating temperature, and an increase in conductivity by a factor of 10 to 100. The procedure is highly dependent on the doping and composite concentrations. For example, more than 10 mol%  $\text{MF}_x$ -doped  $\text{LaF}_3$  ( $\text{M} = \text{Na}, \text{Ba}, \text{Ca}, x = 1, 2$ ) usually has a lower conductivity than pure  $\text{LaF}_3$ , and  $\text{Al}_2\text{O}_3$ - $\text{LaF}_3$  composites also decreases the conductivity of  $\text{LaF}_3$ . These effects may be due to the fact that pure  $\text{LaF}_3$  already has a high lattice defect concentration. However, many fluorides have been successfully doped, e.g.,  $\text{NaF}$ - $\text{MF}_2$ - $\text{Al}_2\text{O}_3$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ),  $\text{BaF}_2$ - $\text{Al}_2\text{O}_3$  and  $n\text{MF}_x$ - $\text{LaF}_3$  ( $\text{M} = \text{Na}, \text{Ca}, \text{Sr}, \text{Ba}, x = 1$ – $2$ , and where the  $n$  is less than 0.1.). Figs. 1 and 2 show the  $I$ - $V$  characteristics (Fig. 1(a)Fig. 2(a)) and corresponding resistance and conductivity (Fig. 1(b)Fig. 2(b)) of the  $\text{NaF}$ - $\text{CaF}_2$ - $\text{Al}_2\text{O}_3$  and  $\text{BaF}_3$ - $\text{Al}_2\text{O}_3$  electrolytes. In the  $I$ - $V$  characteristics, the linear section in the central region reflects the IR loss mainly caused by the electrolyte, from which the resistance, and thus the

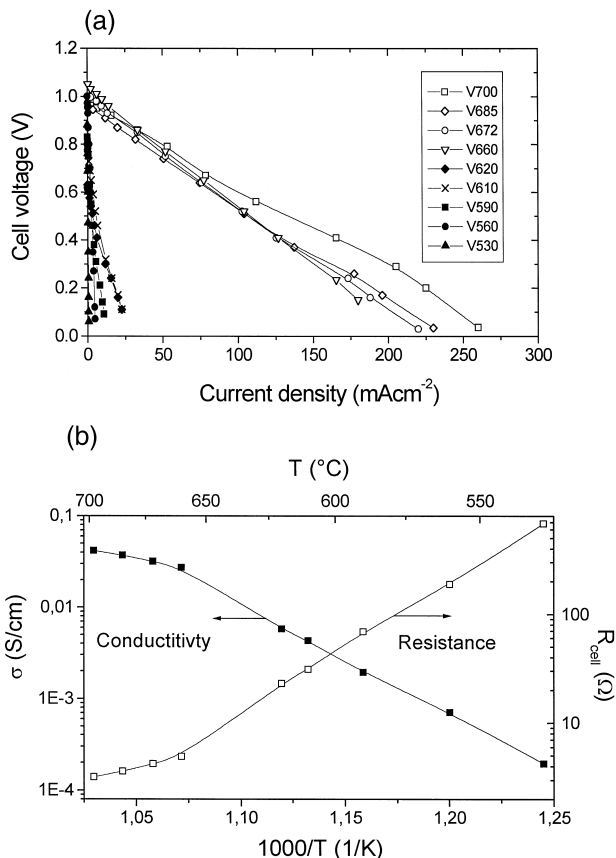
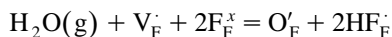


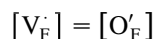
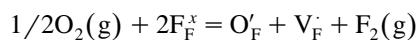
Fig. 1. (a) *I*-*V* characteristics for the NaF-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FC measured at various temperatures, with measured temperature indicated, e.g., V700 means the cell voltage measured at 700°C, etc.; (b) temperature dependence of the resistance and conductivity for NaF-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> electrolyte.

conductivity of the electrolyte can be calculated, as shown in Figs. 1(b) and 2(b).

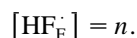
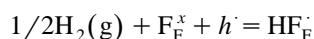
Under FC operation product, water was observed on both sides in some cases, but usually water appeared on the air (cathode) side, indicating that oxide ion conduction is less likely to occur and proton conduction dominates in these electrolytes. Relating results on proton and oxide ion conduction in fluorides have been reported elsewhere [10]. The following defect chemistry has been proposed to explain proton and oxygen ion conduction in fluorides at high temperatures [10]. In H<sub>2</sub>O:



in O<sub>2</sub>:



in H<sub>2</sub>:



Both proton and oxide ion conduction are possible in fluoride-based FCs, but proton conduction predominates, since water is mainly produced at the FC cathode. Proton conduction in fluorides may be understood by supposing that larger numbers of interstitial F<sup>-</sup>(i) ions in the fluoride defect structure can become proton carriers by forming H<sup>+</sup>-F<sup>-</sup>(i) dipoles. Protons are able to move from one F<sup>-</sup>(i) site to another, aided as necessary by static lattice F<sup>-</sup>(s) ions. Therefore, fluorides with a highly defect structure will be effective proton conductors.

### 3.2. Electrode effects

A wide range of possible materials was studied to improve FC performance, and to increase the compatibility and stability between the electrodes and M<sub>x</sub>F-based electrolytes, as well as to reduce costs. Among metal electrodes, the Pt/Ag pair for the anode/cathode was more effective than Pt/Pt. Fig. 3 shows the temperature dependence of the open circuit voltages (OCVs) for the M<sub>x</sub>F electrolyte FCs using the Pt/Ag electrode pair. At *T* > 500°C, most pure fluoride electrolyte FCs started to function, giving the expected OCVs between 1.0 and 1.2 V, and only at *T* > 600°C can significant current be drawn. Fig. 4 shows the *I*-*V* characteristics for various pure fluoride electrolyte FCs with the Pt/Ag electrode pair. The

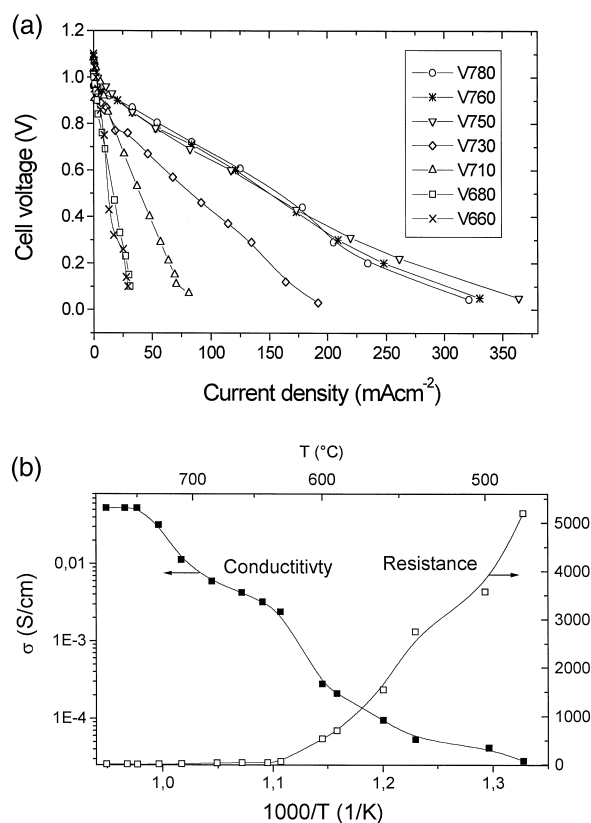


Fig. 2. (a) *I*-*V* characteristics for the BaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FC measured at various temperatures; (b) temperature dependence of the resistance and conductivity for BaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> electrolyte.

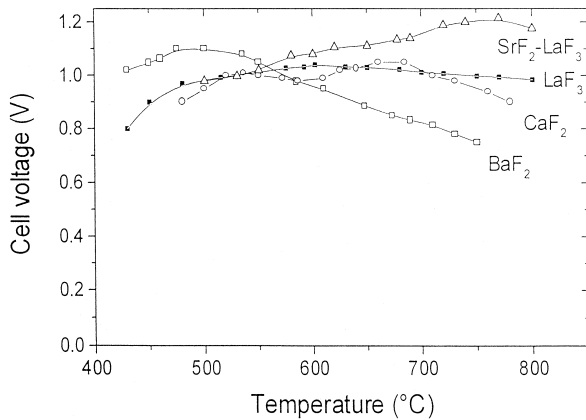


Fig. 3. Temperature dependence of OCVs for pure fluoride electrolyte FCs using the Pt/Ag electrode pair.

best result, about 40 mA/cm<sup>2</sup> at short circuit, was achieved for a LaF<sub>3</sub> electrolyte FC at 700°C. However, the Pt electrode is expensive, and practical FCs need to be constructed using composite oxide anode and cathode, expected to improve the FC performance. The difficulty in the construction is that, due to the incompatibility between composite electrode and M<sub>x</sub>F-based electrolytes, a separation of the composite electrode and the electrolyte often occurs during heat-treatment. This did not happen with the LiNiO<sub>2</sub>-supported cell. Careful control of the sintering process (temperature, time and heating steps) allowed formation of a dense well-characterised ceramic bilayer or FC disc. Fig. 5 shows results for LaF<sub>3</sub> electrolyte FCs with various electrode materials at 700°C. The LiNiO<sub>2</sub> composite anode/LaF<sub>3</sub> bilayer either with pasted Ag, or oxide (Co<sub>2</sub>O<sub>3</sub> or LiCoO<sub>2</sub>) cathode, exhibited better FC performance than that obtained using the Pt/Ag electrode pair. This improvement is much more significant at low temperatures, as shown in Fig. 6. It can be seen from Figs. 5 and 6 that the short circuit current was increased from 40 to 108 mA/cm<sup>2</sup> at 700°C, and from 5 to 85 mA/cm<sup>2</sup> at 580°C for LiNiO<sub>2</sub>/Ag, compared with Pt/Ag. This could

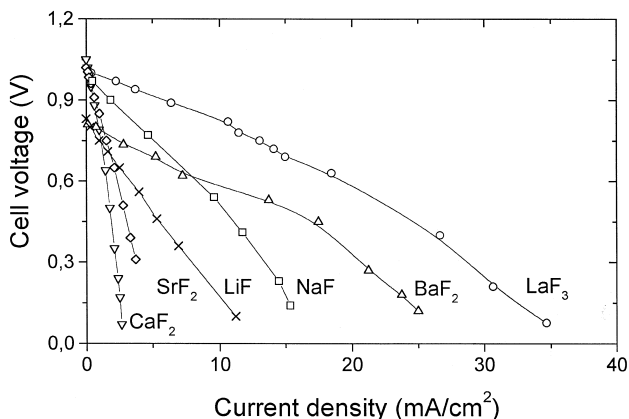


Fig. 4. *I*-*V* characteristics for pure fluoride electrolyte FCs using the Pt/Ag electrode pair at 700°C.

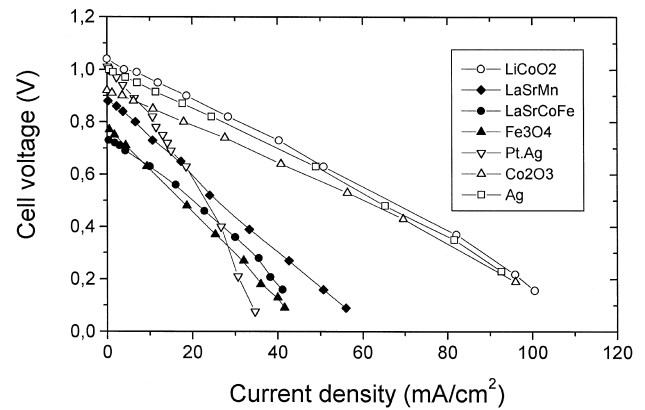


Fig. 5. *I*-*V* characteristics for pure LaF<sub>3</sub> electrolyte FCs using various electrodes at 700°C.

be explained in the following way: thermal activation at low temperatures is insufficient to permit ions to cross over the electrode/electrolyte interfaces. The composite electrode can efficiently increase the exchange current between electrode and electrolyte due to improved interfacial contacts; whereas at high temperatures, a good contact is achieved by thermal activation. The composite electrode technique is thus less able to improve performance at high temperature. In addition, the total current is much larger for LiNiO<sub>2</sub>/Ag electrode pair than for Pt/Ag, indicating that the composite electrode technique can improve contact at the interfaces, resulting in higher exchange currents and better FC performance (cf. Figs. 5 and 6). In addition, it is also interesting that the LiMO<sub>2</sub> (M = Ni, Co) and Co<sub>2</sub>O<sub>3</sub> electrodes have shown much better FC performance than the perovskite electrodes, La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>3</sub> and La<sub>x</sub>Sr<sub>1-x</sub>Co<sub>y</sub>Fe<sub>1-y</sub>O<sub>3</sub> (cf. Fig. 5).

### 3.3. FCs with doping and composite fluoride electrolytes

As mentioned above, the doping and composite effects are highly dependent on the preparation, e.g., on the

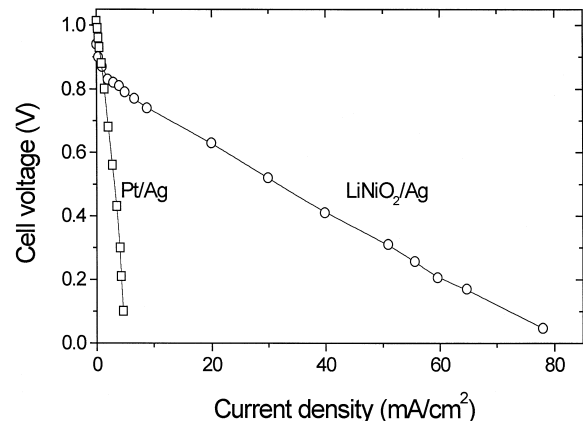


Fig. 6. *I*-*V* characteristics for FCs using LaF<sub>3</sub>-based electrolytes and LiNiO<sub>2</sub>/Ag and Pt/Ag electrode pairs at 580°C.

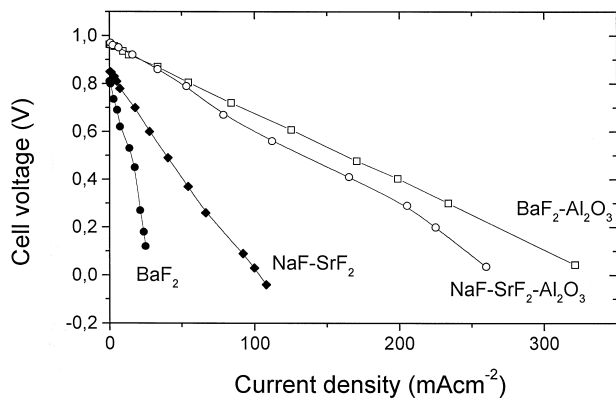


Fig. 7.  $I$ - $V$  characteristics for FCs using NaF-SrF<sub>2</sub>, NaF-SrF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, BaF<sub>2</sub>, BaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> electrolytes at 750°C.

composition, type of dopant and its concentration. Careful control of the dopant and Al<sub>2</sub>O<sub>3</sub> composite concentration has proved successful for many of the fluorides studied. The current output from most doped or composite electrolyte FCs has been enhanced by up to an order of magnitude compared with those using pure fluoride electrolytes. Some results are shown in Fig. 1(a)Fig. 2(a), which may be compared with Fig. 4. Fig. 7 shows  $I$ - $V$  characteristics of FCs using doped MF<sub>x</sub> and composite electrolytes, with pure BaF<sub>2</sub> as electrolyte inserted for comparison. As seen in Fig. 7, a current density of 200 mA/cm<sup>2</sup> at 0.4 V was measured for the BaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> electrolyte FC at 750°C. At the same temperature and voltage only 20 mA/cm<sup>2</sup> was obtained by using pure BaF<sub>2</sub> as the electrolyte. These results demonstrate that the use of doping and composite is indeed a powerful method of improving the properties of fluoride electrolytes and their FC performance, since the doping may improve the fluoride defect structure, and the composite may enhance the ionic conductivity. Further studies will be carried out using tape casting to scale up the disc type FC to a larger area for a practical FC device/stack.

### 3.4. Further improvement of FC performance

It can be seen that the fluoride-based electrolyte FCs studied here have shown a large polarisation loss during operation. It may be caused by the low concentration of the source ions, i.e., protons or oxide ions in the electrolytes, and their low transport in the electrode reaction and FC process. How to increase the source ionic concentration in the fluoride electrolyte, and how to enhance the ionic transport properties thus become key issues in developing practical FC devices using fluoride-based electrolytes. Hydrofluorides may provide a solution. By using lithium-barium fluoride containing about 10 mol% hydrogen as the electrolyte, the FC performance was significantly improved. A short circuit current close to 1000 mA/cm<sup>2</sup>, and a peak power of about 180 mW/cm<sup>2</sup> at 300 mA/cm<sup>2</sup> and 0.6 V have been obtained so far for

dilute reactants, 2% O<sub>2</sub> in Ar as the oxidant and 50% H<sub>2</sub> in N<sub>2</sub> as the fuel [19]. Further development is under progress.

## 4. Remarks and conclusions

It should be mentioned that the above FCs were of the pellet (disc) type (cf. bulk electrolytes). If film ceramic membranes, similar to Li<sub>2</sub>SO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> [20], can be used a significant improvement in the FC performance would be expected. Although there are some difficulties for present fluoride-based FCs, as discussed in Section 3.4, the new systems presented in this paper have a number of advantages over conventional SOFCs. For example, these new types of FCs are easy to construct and operate, using highly cost-effective materials and technology; intermediate temperature (400 to 800°C) allows the use of ordinary metals as interconnectors, current collectors, and sealing materials for the FC stacks and subsystems. Most fluorides are quite inexpensive and have many similarities to oxides, e.g., a high melting point (1760 K for LaF<sub>3</sub>), strong mechanical properties, water resistance, good chemical stability, adequate conductivity, and compatibility with other cell components studied. Therefore, the development of these new systems may directly benefit from the well-developed SOFC technology. As pointed out above, these FCs have only been investigated using bulk electrolytes, without any of the technological improvements needed for practical devices. These include porous, dense ceramic membrane technologies which have proved successful in the development of SOFCs. Thanks to more work devoted to these fluoride-based electrolyte FC systems, a new advanced FC technology with a promising commercial future may emerge. This is the goal of current R&D.

## Acknowledgements

Part of the experiments were carried out by Dr. Bengt-Erik Mellander's group, Chalmers University of Technology, Sweden, acknowledged with gratitude. The author would also like to thank Prof. Pehr Björnbom, Royal Institute of Technology, for his kind help in this research. Thanks are also expressed to Prof. Guangyao Meng, University of Science and Technology of China (USTC), for providing materials and co-operation. This work is supported by the Swedish Research Council for Engineering Sciences (TFR) and Göteborg Energy AB's Research Foundation. Part of the work was also supported by the National Nature Science Foundation of China (NSFC) through the co-operative research in USTC.

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