

Advantages of intermediate temperature solid oxide fuel cells for tractionary applications

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Abstract

Our recent achievements suggest that intermediate temperature (IT) solid oxide fuel cells (SOFCs) can become a strong competitor not only for stationary power generation, but also for tractionary applications, e.g. for electrical (hybrid) vehicles. These ITSOFCs are based on ceria-salt composite ceramic materials. These new ceria-based composite ceramic materials have shown a super ionic conductivity ($0.1\text{--}1.0\text{ S cm}^{-1}$) in the IT region ($400\text{--}600^\circ\text{C}$). Using them as the electrolytes the ITSOFCs are operated between 300 and 1500 mA cm^{-2} ($200\text{--}700\text{ mW cm}^{-2}$) continuously between 400 and 600°C . The opportunities and advantages of these new advanced ITSOFCs for electrical vehicle applications are discussed. The high efficiency ITSOFCs fed directly with hydrocarbon containing gas-type and liquid-type fuels have shown an enormous potential for application in electrical vehicles. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. Background

In May 1999, a joint venture between BMW (a Germany Car Company) and DELPHI automotive systems (the largest automotive supplier in the world) on solid oxide fuel cell (SOFCs) was issued. It aims at developing an entirely new type of fuel cell capable of generating electricity out of petrol at a temperature of about 800°C . Fitted in BMW passenger cars, the SOFC will serve to supply electric energy to the on board network, thus, doing the job for which it is most suitable: generating electricity at a high level of efficiency and operating independently of the engine. This technology should come out in 5 years.

Only a few years ago the on board SOFC technology was a big argument due to the high temperature request. Intermediate temperature ($400\text{--}600^\circ\text{C}$) fuel cells (ITFCs) on board technology shows good perspectives since it, in principal, meets the same demands, but requires simpler system compared to high temperature SOFCs. On the other hand, in comparison to PEFCs (polymer electrolyte fuel

cells) operating with logistic fuels, ITFCs or ITSOFCs show unique advantages due to high ionic transport and fast electrode kinetics in the IT region and do not require noble catalysts.

In September 99, DOE (Department of Energy), USA announced an investment of 24 million US dollars to begin developing ultra-low cost ceramic oxide fuel cells for promoting SOFCs into the market.

Operation on liquid fuels would assist a more rapid introduction of fuel cell technology into the commercial market, because it would greatly simplify the on-board system as well as reduce the infrastructure needed to supply fuel to passenger cars and commercial fleets. The large potential market for fuel cell vehicle applications has generated a strong interest in a fuel cell that can run directly on methanol. It is also more preferable to directly run ethanol or even gasoline. Direct ethanol fuel cells operating at intermediate temperatures are attracting interest because of the highly efficient electrode kinetic and internal reforming processes in the IT region.

1.2. Fuel cell powered electrical (hybride) vehicles

Quick start and temperature management for SOFC powered electrical vehicles are always more critical compared to

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those run by batteries and PEFCs. Today, there is much discussion about how to combine the present batteries or super capacitors with fuel cells to drive electrical vehicles, thus, providing a fast start up. It would not make much difference if the battery or super capacitor is combined with PEFCs or ITSOFCs. The issues and problems to be solved are rather the same. On the other hand, based on our recent achievements, the ITSOFCs proposed here require operating temperatures around 400–500°C. For the elevated operational temperature, say up to 200°C, the PEFCs and DMFCs (direct methanol PEFCs) are always subject to further development in order to overcome the carbon monoxide (CO) poison and methanol cross-over, as well as to enhance the operating efficiency [1–4]. A number of teams have tried to develop new electrolytes by using polymer-oxide organic-inorganic composite electrolytes or other composite polymer electrolytes for higher temperature operation [1–4]. Our new composite ceramic electrolytes have demonstrated interesting results for SOFCs in the IT region. Further lowering of temperature can be realised by improving the catalysts and electrodes. The future trend would result in a very close operating temperature range for PEFC and SOFC powered electrical vehicles. It may also be realised that during the vehicle parking period the temperature (400–500°C) of the ITSOFCs would be easily maintained by electricity heating from the super capacitor self-discharge or battery discharge to compensate the heat loss from the thermal insulation of the fuel cells.

The conventional SOFCs face another technical challenge since the brittle ceramic components may be easily cracked in the moving vehicles. This difficulty becomes less serious in the present SOFC technology due to the development of thin film electrolyte and nickel-foam electrode support. Furthermore, our ITSOFCs are based on new composite ceramic materials, which have combined elastic components with the oxides to avoid the cracking problem, thus, improving the durability of the ceramic components.

In the last years our efforts have been addressed to the development of new materials and technology for ITFCs (including ITSOFCs) [5–10]. Recently ITSOFCs using new ceria-based oxide-salt ceramic composites have been developed [11].

2. Experimental

2.1. Materials and preparation

The following materials were used for the cell construction: (i) electrolytes: commercial $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) powder was purchased from Seattle Specialty Ceramics, USA. The alkaline hydroxides, e.g. MOH (M = Li, Na), alkaline/alkaline earth halides, e.g. MX_i (M = Li, Na, Ca, Sr, Ba; X = Cl, F; i = 1, 2) (A.R., Aldrich Chemical Company Inc., USA) were used to prepare various composites with GDC or SDC; (ii) electrodes of the type NiO (Merck,

A.R.) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF) (Seattle Specialty Ceramics, Seattle, WA, USA). The silver (Leitsilber 200, Hanau, Germany) paste covered on the electrodes was used as the current collector. Stainless steel was adopted for the fuel cell device holder.

The composite samples were prepared by mixing GDC with one of the above-mentioned salts in a weight ratio from 10 to 20% of the total weight and grounded well. The mixtures were heat-treated at 700°C for 1 h. The resulting materials were ground thoroughly for use. The samples with the fluoride components were heat-treated for a second time. More detailed information on the sample preparation and materials are provided in an international PCT patent application [11].

2.2. Fuel cell construction

ITSOFCs were constructed using the composite anode-supported technique. A composite anode was made by a mixture of electrolyte (40 vol.%), anode, e.g. GDC- or SDC-NiO composite, (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. The composite electrode-supported fuel cells were constructed by directly pressing the anode, electrolyte and cathode in one step. The cathode was prepared as the composite form in a similar way to that of the composite anode in replacement of NiO by the LSCF. To avoid cracking and separation of the fuel cell components (anode, electrolyte and cathode) during heating, complete fuel cell assemblies were heat-treated using a program-controlled furnace to carefully adjust the temperature rise and holding time, e.g. for 30 min at 600°C.

The fuel cell assemblies after heat-treatment were pasted by the silver paste on both electrodes used as the current collectors, then mounted into the fuel cell device with the following configuration.

Anode (fuel chamber)/electrolyte/cathode (oxidant chamber), the cell size normally being 13 mm in diameter and 1.0–2.0 mm thick. The fuel cell device is schematically drawn in Fig. 1. The fuel was a hydrogen, hydrocarbon gas-type (methane mixed with hydrogen) or liquid-type (e.g. methanol and ethanol) and the oxidant was air. The gas flows were controlled between 10 and 50 ml/min under 1 atm

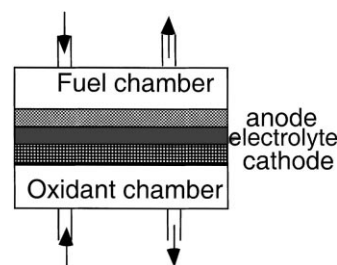


Fig. 1. A schematic of the fuel cell testing device.

pressure. All gases were directly fed into the fuel cell chambers without preheating. The liquid fuels, e.g. methanol and ethanol, were fed by the syringe pump through the tubular evaporator (about 180°C), and then became gas-type to the fuel cell device in operation.

The fuel cell devices were demonstrated in this work using the laboratory types, which is, at this stage, not able to make the analysis of the fuel utilisation.

2.3. Characterisation

Material characterisation of the electrical properties was carried out using a.c. impedance analysis. The impedance analysis was performed with a computerised Hewlett-Packard HP4274A LCR-meter. The measured frequency range covers from 0.1 Hz to 100 kHz with an applied signal of 20 mV. The temperature of the sample (holder) was controlled by an Eurotherm temperature controller and the sample temperature was measured with a platinum thermocouple attached at the position of the sample. In most cases, the measurements were carried out between 400 and 600°C.

Electromotive forces (EMFs) were measured using a Schlumberger Solartron 7150+ digital multimeter or a Keithley 616 electrometer with an input resistance of 1012 or 1014 Ω . I - V characteristics and other fuel cell performance were determined by using a computerised equipment for measuring current and voltage under variable loads. The temperature of the fuel cell was controlled by an Eurotherm temperature controller, and the temperature of the sample was measured with a platinum versus platinum-10% rhodium thermocouple attached close to the sample.

3. Results and discussion

3.1. Electrolyte properties and fuel cell performances

Ionic conductivity of the ceria-salt composite ceramic electrolytes was measured in the range of 0.1–1.0 S cm^{-1} at intermediate temperatures. This conductivity value is 10^4 times higher than that of the zirconia-based electrolytes for HT (high temperature, above 800°C) SOFCs and 10–100 times higher than that of the conventional ion-doped ceria at the same temperatures. These new materials have also overcome the chemical stability problem for the conventional ceria-based electrolytes. These highly conducting new composite ceramic materials create a great potential for commercialising ITSOFCs. The success in continuous R & D of these new materials and novel ITSOFCs will lead to new fuel cell areas, correspondingly changing the strategy of R & D for SOFCs, and accelerating the SOFC commercialisation.

Fig. 2 shows typical current and power density versus voltage, i.e. I - V (I - P) characteristics, at different tempera-

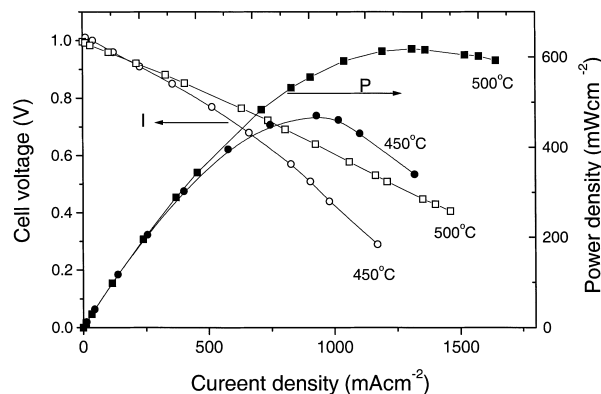


Fig. 2. Typical I - V characteristics for the ceria-salt composite ceramic electrolyte SOFCs at different temperatures. Fuel: H_2 plus 10% CH_4 ; oxidant: air; pressure: 1 atm; flow: 30–50 ml/min.

tures for the new composite ceramic electrolyte ITSOFCs in presence of the hydrogen mixed with 10% methane as the fuel. As can be seen from Fig. 2, the cell reaches a max. power density of around 500 and 600 mW cm^{-2} at 450 and 500°C, respectively. The ITSOFCs using these new composite ceramic electrolytes were operated between 300 and 1500 mA cm^{-2} (200–700 mW cm^{-2}) continuously between 400 and 600°C. Table 1 lists some typical ITSOFC performances at various temperatures in presence of the hydrogen fuel. The highest power density of 718 mW cm^{-2} (1200 mA cm^{-2}) at 600°C has been reached so far. Without any further technical improvement the fuel cell performance was stable and experienced more than hundreds of hours life test. Under the speeded-up testing conditions, i.e. the operation with the heavy loads, the fuel cells were operated constantly for several 10 h with the power density output around 600 mW cm^{-2} corresponding to the current density output, around 1000 mA cm^{-2} at 600°C, as shown in Fig. 3. These results favourably compared to those observed up to now with SOFC technology in the IT region. The evaluation on the electrochemical characteristics for various fuels, e.g. CH_4 and its different concentrations in the hydrogen mixed fuels and other hydrocarbon fuels, etc. will be further studied.

Without any efforts in developing new catalysts for the liquid fuels and using just the same electrodes for the regular

Table 1

The performance at various temperatures obtained from the composite ceramic ITSOFCs^a

Temperature (°C)	(mW cm^{-2})
420	380
450	460
500	590
530	620
560	650
580	680
600	718

^a Fuel: H_2 ; oxidant: air; pressure: 1 atm; flow: 10–50 ml/min.

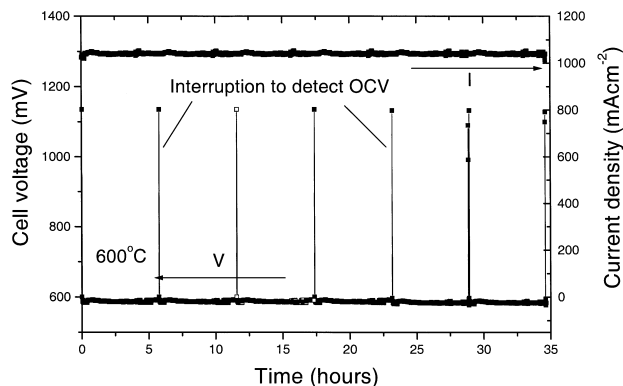


Fig. 3. Discharging performance of a typical ITSOFC using the ceria-salt ceramic composite electrolyte operated at 600°C. Fuel: H₂; oxidant: air; pressure: 1 atm; flow: 30–50 ml/min.

ITSOFCs the fuel cell devices showed around the OCV 0.95 V for the 2 M methanol, 0.91 V for the 1 M ethanol (Fig. 4) and 0.78 V for the 1 M acetone at 600°C. Using directly these liquid fuels, the ITSOFCs were operated under 300–450 mA cm⁻² (180–280 mW cm⁻²) at 600°C with a peak power density around 330 and 300 mW cm⁻² for the methanol and ethanol fuel cells, respectively, see Fig. 4. These performances are comparable with those of advanced DMPEFCs [1,2]. The performance of the liquid fuelled ITSOFCs can be certainly improved greatly by developing suitable catalysts as demonstrated for DMPEFCs. For example, very recently the CuO was found to be very active for the direct liquid ceramic fuel cells. The CuO additives in the electrodes can significantly promote the electrode reaction for methanol and ethanol, and improve the DMSOFCs (direct methanol SOFCs) and DESOFCs (direct ethanol SOFCs) performances. Further study on this subject is under progress.

Although methanol has shown better fuel cell performance, there are some advantages to use ethanol over

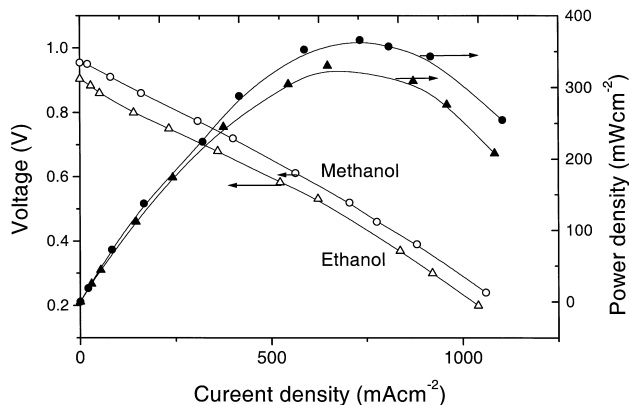


Fig. 4. Typical ITSOFCs using the ceria-salt ceramic composite electrolyte, and methanol and ethanol fuels operated at 600°C. Fuels: 2 M methanol, and 1 M ethanol; oxidant: air; pressure: 1.5 atm of the methanol or ethanol back pressure, and 1 atm for the oxidant (air).

the methanol fuel, since methanol is highly corrosive and more volatile than ethanol; furthermore the methanol vapour is also highly toxic. With no doubt the IT operation provides benefit, for the liquid fuelled fuel cells, especially in terms of lower catalyst cost and better electrode reaction efficiency.

3.2. Advantages for proposed ITSOFCs compared with PEFCs for electrical vehicles

The new advanced ITSOFCs have unique advantages of operation with hydrocarbon gas-type and liquid-type fuels without the need of using noble catalysts. These achievements have shown a great interest and economical potential in developing new generation fuel cell technology for the electrical vehicles. The ITSOFCs are surely a new candidate and capable competitor for the electrical vehicle in comparison to the PEFCs.

ITSOFCs may be superior to PEFCs in the following respects:

- High temperature (400–600°C compared with PEFCs, 80–150°C) operation allowing to get higher electrochemical efficiency.
- ITSOFCs have no CO poison problem at all. The carbon monoxide is actually the fuel operated for the ITSOFCs.
- There is no need for noble Pt catalyst in ITSOFCs. The usage of Pt catalyst is, in fact, a drawback for future PEFC electrical vehicle industrialisation due to very limited Pt resource in the world, in addition to expensive cost as well. On the contrary, the ITSOFCs are based on materials which have abundant and inexpensive natural resources.
- There is no need for reformer as carbon containing fuels can be directly fed into the ITSOFCs allowing direct reforming mechanism to occur in the electrode chamber. On the other hand, the reformer is a size dependent reactor, which is hardly compatible with a module type fuel cell construction. Therefore, the non-reforming ITSOFC technology favourably compares to the reformer-based PEFCs.
- The ITSOFCs can be directly operated with many fuels, such as natural gas, various hydrocarbon fuels and liquid fuels, e.g. methanol and ethanol; while the PEFCs are limited seriously by the fuel.
- The manufacturing cost and final product price for the ITSOFC would be much cheaper than that of the PEFC, since low cost metals and ceramics are used for the bipolar plates and cell components.

In addition, the carbon deposition can be effectively avoided in the IT region, as compared to the conventional SOFCs with high temperatures (above 800°C) operation, which easily causes carbon deposition for using the hydrocarbon fuels, such as methane etc. Therefore, for the on board technology with the carbon containing liquid fuels, such as methanol and ethanol, intermediate temperature operation and ITSOFC technology are preferable.

4. Conclusions

In summary, novel advanced ITSOFCs have demonstrated. These systems have a great potential and many advantages for both stationary and tractionary applications. Methanol and ethanol can be suitably employed in ITSOFC technology for the electrical (hybride) vehicles. Accordingly advanced ITSOFCs possess properties and advantages to become an able competitor. Therefore, in the author's opinion, the development of novel ITSOFCs for market applications is imminent. It is believed that the ITSOFC industrialisation will have thorough social impact and will create new high economic developing areas.

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