Solid-State Proton Conductors

Final Report

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EXECUTIVE SUMMARY

The purpose of this program was to survey the field of solid-state proton conductors (SSPC), identify conductors that could be used to develop solid-state fuel cells suitable for use with coal derived fuel gases, and begin the experimental research required for the development of these fuel cells. An up-to-date review of SSPC literature was conducted and perovskite oxides as a group were identified as the most promising. A rationale for the selection of likely SSPC perovskite materials was developed which was based on comparison of electronic states of the respective elements in a particular formulation and the length of the edge of the respective unit cell.

The validity of this method was confirmed by correlation predictions with existing data for known perovskite proton conductors. The method was then used to identify the most likely candidates for high protonic conductivity. Barium cerium oxide was identified as the best candidate of those known to be proton conductors and barium thorium oxide was identified as potentially being the best SSPC possible of known perovskite compounds.

During the experimental work, a novel apparatus for measuring proton conductivity was assembled. This apparatus not only provided for a wide range of oxidizing and reducing gas compositions to be supplied to the cathode and the anode but also allowed the outer edges of the SSPC electrolyte disk to be surrounded by a controlled atmosphere. This capability proved to be crucial to developing an understanding of the impact of water vapor on proton conductivity. This apparatus was used to evaluate the SSPC capability of a commercially prepared electrolyte disk of Yb-doped strontium cerium oxide. The ionic conductivity of this material is well known although there is some question in the literature as to whether it is a true proton conductor. The results obtained confirmed the utility of the apparatus and the suitability of the measurement technique and experimental protocol. In a series of experiments performed with solid palladium electrodes, hydrogen was pumped from a hydrogen containing atmosphere into a dry inert gas, confirming that strontium cerium oxide transports hydrogen. Furthermore, the ionic conductivity of the disk measured with this apparatus was within experimental error of that quoted in the literature, adding further support to the hypothesis that this material is a proton conductor and eliminating oxide ion conduction as a major contributor to the ionic conductivity.

Next, several attempts were made by a commercial lab to prepare thin, sintered disks of neodymium doped barium cerium oxide and barium thorium oxide by hot pressing powders at temperatures up to 1750°C. These attempts, however, met with failure. A method was developed at the Institute of Gas Technology (IGT) for preparing disks of neodymium doped barium cerium oxide by cold pressing the powder with an organic binder and then sintering in air at 1600°C. Samples having a density in excess of 97% theoretical density were obtained. When the same methods were applied to the barium thorium powder, however, a crack-free sample could not be produced.

Two configurations were used in evaluating the barium cerium sample. In one, solid palladium electrodes which are permeable to hydrogen, were applied to both surfaces and hydrogen transport was confirmed. Both the chemical composition and the ionic conductivity were found to be stable in highly oxidizing and highly reducing atmospheres. An ionic conductivity of $9.3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ was measured for this sample at 850°C. A problem developed in that gases built up at the anode/electrolyte interface and separated the electrode from the electrolyte. The origin of these gases could not be determined; however, it is probable that this sample has some small amount of oxide ion conductivity that contributed to the production of water vapor at the anode/electrolyte interface. As a consequence, a second cell was prepared using porous palladium electrodes. Although this cell suffered from poor contact between the electrolyte, the porous electrodes and the platinum current collectors, it provided the data necessary to confirm proton conductivity at 700°C and mixed ionic conductivity, probably proton and oxide ion, at 800°C.

In summary, this program successfully demonstrated that SSPC fuel cells can be fabricated from perovskite oxides by practical methods and identified Nd-doped barium cerium oxide, a stable proton conductor with low electronic conductivity, as a leading candidate for the development of SSPC fuel cells for use with coal derived fuel gases.

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1.0. INTRODUCTION

Proton conductors are a kind of ionic solid conductor in which the movement of H^+ ions is responsible for charge transfer. Recently, solid-state proton conductors (SSPC) have drawn particular attention because of a wide range of possible applications;¹ a few of which are presented in Figure 1. SSPC have been applied in fuel cells,²⁻¹¹ steam electrolyzers,^{5,4,12-16} gas sensors,^{17,18} electrochromic displays,¹⁹ etc. They are also a promising material for batteries and hydrogen storage applications.¹ The hydrogen could be extracted from a gas mixture²⁰ and stored directly (for example, in the form of metal hydrides.)²¹ This review discusses the current state-of-the-art of SSPC with special emphasis on fuel cell applications in the temperature range of 400° to 800°C. The basic principles of SSPC fuel cell operation are presented in Figure 2 together with electric potential relationships within the cell. SSPC fuel cell is a relatively new area of interest in comparison with other, more advanced technologies, such as alkaline fuel cell (operating at 50° to 150°C), phosphoric acid fuel cell (operating at 150° to 200°C), molten carbonate fuel cell (operating at 600° to 700°C) and solid oxide electrolyte fuel cell (operating at 800° to 1000°C). Some advantages of SSPC fuel cell operation are listed below:

- There is no liquid present in the electrochemical cell. This eliminates some problems typical for systems with liquid electrolyte (corrosion, leakage, pore flooding, maintaining the three-phase boundary, etc.)
- Protonic conductors can be used as thin films in order to reduce ohmic losses. Thin film techniques and other methods developed for oxide ion conductors are also applicable in this system to some extent as well.
- A wide range of different fuels could be used: $CH_4 + H_2O$, C_2H_6 , $CO + H_2O$, H_2 , etc.
- Water vapor is produced at the cathode (air electrode) not at the anode as it is in the solid oxide-ion fuel cell. Additional fuel circulation may not be needed.
- SSPC systems can work in both fuel cell and steam electrolysis regime.
- Wide range of cogeneration processes may be possible producing chemicals through dehydrogenation with simultaneous electric current production.

Figure 1. SOME OF THE SSPC APPLICATIONS
(Modified After Jensen¹)

anode: $\text{H}_2 = 2\text{H}^+ + 2\text{e}$

cathode: $2\text{H}^+ + 0.5 \text{O}_2 + 2\text{e} = \text{H}_2\text{O}$

Figure 2. PRINCIPLES OF SSPC FUEL CELL OPERATION AND ELECTRIC POTENTIAL RELATIONS AT OPEN CIRCUIT VOLTAGE (-) AND UNDER LOAD (...) -- SIMPLIFIED PICTURE
(E-Open Circuit Voltage, U-Cell Voltage, ΔV -Overpotential, ϕ -Potential, A-Anodic, C-Cathodic)

The main problems at the present stage of the SSPC fuel cell system development are:

- High ohmic losses (due to relatively low ionic conductivity of protonic electrolytes)
- High cathode polarizations.

In the following section, current status of SSPC fuel cell technology is discussed with particular emphasis on the problem of protonic conductor electrolytes. Increasing the conductivity seems to be the key to fuel cell applications in the temperature range of 400° to 800°C. The relatively small conductivity level of the state-of-the-art protonic conductors limits practical application of this technology. Problems related to electrodes (especially cathode) for SSPC fuel cells are also described along with techniques applicable for SSPC fuel cell investigations and fabrication.

2.0. HISTORY OF DEVELOPMENTS AND CURRENT STATUS OF THE SSPC

2.1. Review of Proton Conducting Electrolyte Structures

In general, SSPC contain discrete proton energy levels, residing at a considerable distance from one to another. The mobility of H^+ in these solids is thought to be due to the hopping and/or quantum mechanical tunneling along the hydrogen bonds,²²⁻²⁵ followed by rotation of the H_2O , NH_3 , OH^- , or other group (Grotthus mechanism). More recently, a "vehicular" mechanism was proposed.^{26,27} In this model, OH_3^+ or NH_4^+ ions are considered to be mobile, rather than H^+ . In other words, the proton is carried by H_2O or NH_3 molecules acting as vehicles. A consequence of this mechanism is the requirement for a vehicle molecule at the anode and its liberation at the cathode.²⁸ Both theories have advantages in restricted fields and as yet no general model for proton transport in solids has emerged.²⁷

At lower temperatures, proton conduction is usually strongly dependent on the degree of hydration of the material. Liberation of water molecules at higher temperatures leads to conductivity loss, and sometimes an unusual conductivity dependence versus inverse temperature is observed. For fully protonic conductors, the specific conductivity, σ , can be described by:

$$\sigma = N z e \mu \quad (1)$$

where "N" is the number of mobile particles per unit volume, μ their mobility, and "ze" is their charge. The diffusion coefficient is related to conductivity by the Nernst-Einstein equation:

$$\frac{D}{\sigma} = \frac{KT}{e^2 n} H \quad (2)$$

where H is called the Haven ratio and depends on the mechanisms of diffusion and conduction (for the best solid conductors, the mechanisms are similar and $H = 1$). When more than one charge carrier participates in the conduction process, ionic and electronic transference numbers, t_j , should be defined:

$$t_j = \sigma_j / \sum_{i=1}^N \sigma_i \quad (3)$$

$$\sum_i t_i = 1 \quad i, j = e, H^+, O^=, \text{ etc.} \quad (4)$$

A review of protonic conductors and their properties is presented in Table 1.

Table 1, Part 1. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
α -AlOOH	A	<400°C	10	$\sigma_p \sim 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ at 350°C.
Aminophosphates	A	<150°C	10	Aminophosphates melt generally below 150°C. The best conductivities were observed for $\text{C}_6\text{H}_{12}\text{N}_2 \cdot \text{H}_3\text{PO}_4$ (melts at 162°C), $\sigma_p = 2.4 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ at 150°C and for $\text{C}_6\text{H}_{12}\text{N}_2 \cdot 3\text{H}_3\text{PO}_4$ (melts at 127°C), $\sigma_p = 1.1 \times 10^{-6}$ at 150°C.
Aminesulfates	A	<200°C	10, 29,30	Melt generally below 200°C. The best conductivities were observed for $\text{C}_6\text{H}_{12}\text{N}_2 \cdot \text{nH}_2\text{SO}_4$ (TED salts). Compounds with n=1, 1.5 and 2 are formed at room temperature between triethylenediamine and H_2SO_4 . Melting points are: 300°, 320°, and 250°C for n=1, 1.5, and 2, respectively. ¹⁰ Gradual decomposition in air occurs above 220°C. The best conductivity was observed for n=1.5, $\sigma_p = 1.5 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$. ¹⁰ However, Daniel et al. ³⁰ are of the opinion that TED salts can safely be heated up to 150°C under normal pressure but it will be difficult to use higher temperatures for practical applications.
$\text{NH}_4^+ - \text{H}^+ (\text{H}_2\text{O})_n$ b and b" alumina	B	<700°C	28, 31-36	Preparation methods were presented. ^{23,31,32} Studies of thermal decomposition of β'' compound showed irreversible ammonia loss above 200°C. ^{27,28,57} Above 250°C transition spinel forms.

Table 1, Part 2. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
$H^+(H_2O)_n$ 8 and 8" alumina	B	<800°C	37,38	Conductivity at about $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ was measured at 250°C for 8" alumina. Dehydration occurred above this temperature ($n=2 + n=1$).
BPO_4	C	<300°C	12	Drop of conductivity is observed above 150°C in air because of the instability of BPO_4 phase: $2BPO_4 + 6H_2O \rightarrow B_2O_3 \cdot 3H_2O + P_2O_5 \cdot 3H_2O$ More stable in flowing steam at ambient pressure but conductivity doesn't exceed $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 250°C and decreases slowly with further temperature increase.
$Ce(HPO_4)_2$	--	--	40	σ_p (250°C) $\approx 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$
$CsHSO_4$	B	<210°C	41,42	Significant increase in proton conductivity above 141°C results from the phase transition in $CsHSO_4$ crystal. Activation energy for proton conductivity was found to be 0.33 eV in the temperature range 141° to 210°C ($\sigma_p \approx 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 210°C). Above 210°C, thermal decomposition was observed.
$CsHSeO_4$	B	<207°C	41	Similar behavior as for $CsHSO_4$ was observed. Within the temperature range 124° to 207°C, nearly the same activation energy and only a little lower conductivity ($\sigma_p \approx 7 \times 10^{-3}$ at 200°C) were measured. Thermal decomposition occurred above 207°C.

Table 1, Part 3. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
H ₃ BO ₃	A	--	10,43	Relatively high protonic conductivity ($\sigma_p = 0.5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 250°C) in the high-pressure H ₃ BO ₃ phase was reported ¹⁰ in comparison with low conductivity in ambient pressure phase ($\sigma_p = 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$, very low activation energy). Phase transition temperature was a function of pressure (e.g., $T_{tr} \approx 160^\circ\text{C}$ at $p = 7.6 \text{ kbar}$). Examination of high-pressure phase at ambient pressures was carried out. Conductivity loss was observed after a few minutes. A limited, stabilization effect of SO ₄ ²⁻ doping was found.
CsTi ₂ NbO ₇	C	<200°C	44	$\sigma_p < 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at $T > 100^\circ\text{C}$.
H _{0.39} WO ₃ , H _{0.36} MoO ₃ , HTaWO ₆ , H _{1.4} ReO ₃	--	<100°C	45,46	A poor protonic conductivity is expected (based on diffusion coefficients) for all compounds. ⁴⁵ Protonic conductivity, $\sigma_p = 4 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 126°C, was estimated by Slade et al. ⁴⁶ for H _{0.36} MoO ₃ .
H _{1.71} MoO ₃	--	<180°C	46	The NMR study gave a value of activation energy for hydrogen diffusion ($E = 20 \text{ kJ mol}^{-1}$) and correlation time ($t_c \approx 10^{-13} \text{ s}$) typical for fast protonic conductors. Protonic conductivity was calculated using Nernst-Einstein relationship and assuming a Haven ratio of unity ($\sigma_p \approx 2 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 27°C).

Table 1, Part 4. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
$\text{H}_3\text{MO}_{12}\text{PO}_{40} \cdot n\text{H}_2\text{O}$ (MPA) $\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot n\text{H}_2\text{O}$ (WPA)	A	<100°C	5,7, 48,49	High proton conductivities were found in MPA ($s_p = 0.17 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C, $E = 13.7 \text{ kJ mol}^{-1}$). Conductivity was strongly dependent on relative humidity. The MPA $\cdot 29 \text{ H}_2\text{O}$ was stable in temperature range 10° to 80°C over 70% RH. Dehydration of all molecules of water occurred at about 100°C with loss of conductivity. The WPA $\cdot 29 \text{ H}_2\text{O}$ was stable in the temperature range 20° to 80°C above 83% RH. The WPA dehydrates 23 molecules of water around 100°C. The remaining six molecules dehydrate about 200°C. The lack of electronic conductivity in MPA pellet as well as very low gas permeability were reported.
$\text{HfNbO}_3, \text{HTaO}_3$	B	<300°C	47,50	Proton diffusion occurred in both compounds above 130°C. Conductivity measurements gave similar activation energies ($E = 49 \text{ kJ mol}^{-1}$ for HfNbO_3 and 50.5 kJ mol^{-1} in HTaO_3) and low conductivity values ($s_p = 3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ in HfNbO_3).
$\text{HTi}_2\text{NbO}_7 \cdot 2\text{H}_2\text{O}$	C	<200°C	51	Dehydration of the first (21° to 62°C) and second (62° to 220°C) molecule of water was connected with decrease in conductivity. In the temperature range 220° to 260°C, HTi_2NbO_7 decomposed to oxides. Low protonic conductivity was reported ($s_p = 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 200°C).

Table 1, Part 5. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
$\text{HfO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP)	C	<200°C	52-55	Relatively high conductivities at elevated temperatures were found (anisotropic, $\sigma_{\text{max}} = 4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 20°C). Dehydration of water molecules with temperature increase, resulted in conductivity loss. Low conductivity values after complete dehydration were reported ($\sigma_p = 7 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 150°C, $\sigma_p = 8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 250°C. $\sigma_p = 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 20°C. Transition was observed at 28°C (due to dielectric ordering) with conductivity increase ($\sigma_p = 8 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $E = 0.27 \text{ eV}$ at 30°C). Conductivity was strongly dependent on water content. Irreversible dehydration occurred at 97°C. At a high-pressure regime only a slightly increased conductivity was observed up to 2.5 GPa (at room temperature) with significant conductivity loss above this pressure.
$\text{HfO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$	B	<100°C	54, 56	
$\text{Hf}_2(\text{PO}_4)_3$	--	<400°C (cond.)	40, 49	The decomposition of $\text{Hf}_2(\text{PO}_4)_3$ to ZrP_2O_7 and ZrO_2 took place at temperatures higher than 650°C. $\sigma_p = 5 \times 10^{-7}$ at 250°C and $\sigma_p = 5 \times 10^{-6}$ at 400°C.
a-KHF ₂	A	<196°C	24, 43	$\sigma_p = 10^{-7}$ at 196°C. At 196°C, phase transition occurred with conductivity jump about three orders of magnitude. In b-phase current is carried mostly by F^- and K^+ ions. Higher pressures increased protonic conductivity in a-phase ($\sigma_p = 3 \times 10^{-5}$ at 196°C and 3.8 kbar) but did not change significantly a to b phase transition temperature.

Table 1, Part 6. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range		Refs.	Remarks
		Investigated	Range		
$\text{NH}_4\text{H}_2\text{PO}_4$, KH_2PO_4	A	<130°C		10, 58	Conductivities were measured below 130°C. Both single crystals exhibited the one order higher conductivities than polycrystalline pellets ($\sigma = 10^{-7}$ at 100°C for both crystals).
LiH_2PO_4	A	<100°C (cond.)		59	Results of thermal analysis showed weight losses up to 3.5% in the temperature range 30° to 110°C related to moisture removal as well as removal of 0.5 molecules of water in the temperature range 150° to 260°C with final $\text{Li}_2\text{H}_2\text{P}_2\text{O}_7$ formation. Conductivity data were presented up to 100°C for Li_3PO_4 and H_3PO_4 dopings. The highest conductivity at 100°C exhibited $\text{LiH}_2\text{PO}_4 + 5 \text{ wt } \% \text{ H}_3\text{PO}_4$ ($\sigma = 4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 100°C). Li_3PH_4 addition increased activation energy.
NaH_2PO_4	--	20°C		59	$\sigma_p = 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 20°C.
$\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	AC	<400°C		60	Three temperature regions of conductivity were observed: a slight increase in protonic conductivity up to 50°C with maximum ($\sigma_p = 6-7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ about 40° to 50°C) and decrease in conductivity (due to dehydration process) up to 150°C ($\sigma_p = 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at about 150°C). Further increase in conductivity above 150°C was related to K^+ and Sb ions contribution.

Table 1, Part 7. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
H_3O^+ - NGS H_3O^+ - KNKS	B	<100°C	61,62	<p>Polycrystalline proton conductors were fabricated by field assisted ion exchange of H_3^+ for Na^+ in $\text{Na}_5\text{GdSi}_4\text{O}_{12}$ (NGS) and for Na^+ and K^+ in $\text{K}_x\text{Na}_{5-x}\text{GdSi}_4\text{O}_{12}$ (KNKS).</p> <p>Similar activation energies for H_3O^+ - NGS and H_3O^+ - KNKS were observed ($E = 10.68 \text{ kcal/mol}^{-1}$ and $10.9 \text{ kcal/mol}^{-1}$, respectively). Higher protonic conductivity in H_3O^+ - KNKS were measured ($\sigma_p = 1.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$).</p>
KOH (1 m/o K_2CO_3 , 1.3 m/o H_2O)	B	< 410°C	63	<p>Phase transitions were observed:</p> $\alpha\text{KOH} \xrightarrow{248^\circ\text{C}} \beta\text{KOH} \xrightarrow{406^\circ\text{C}} \text{melting}$ <p>A molten KOH + K_2CO_3 phase appeared at 366°C. Absence of temperature hysteresis within the temperature range 248° to 350°C was found. Above that temperature conductivity varied with the thermal history of the sample. Conductivities $\sigma_p = 3.3 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 248°C and $\sigma_p = 2 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 350°C were measured, with activation energy, $E = 53 \text{ kJ mol}^{-1}$. High conductivity at 410°C was related to ionic species other than protons (K^+, OH^-). Weight loss occurred at this temperature. Within the temperature range 248° to 350°C reproducible values of conductivity were observed throughout a period of 9 months. No reaction with Pt electrode was observed unless oxygen was present when film of yellow $\text{K}_2\text{Pt}(\text{OH})_6$ was formed.</p>

Table 1, Part 8. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range		Refs.	Remarks
		Investigated			
M(OH) ₃ , MOOH, M=Y, La, Nd, Sm, Gd	--			64	Protonic conductivities of these compounds were measured in wide temperature ranges. Typical thermal decomposition sequence was found to be: $\text{Gd(OH)}_3 + \text{Cd}_2\text{O}_3 \cdot 1.5 \text{ H}_2\text{O} + \text{GdOOH} + \text{Gd}_2\text{O}_3$ The best conductivities from among the compounds considered were found in Gd(OH) ₃ , $\sigma_p = 5.9 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 250°C and in GdOOH, $\sigma_p = 9 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 400°C. $\sigma_p = 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 207°C.
N ₂ H ₆ SO ₄	--	<210°C		65	
N ₂ H ₆ SbF ₅ N ₂ H ₆ F ₂	A	<110°C < 60°C		66	A conductivity of $\sigma = 10^{-4}$ was measured for N ₂ H ₆ SbF ₅ at 60°C with an activation energy of E = 0.93 eV. The conductivity and activation energy for N ₂ H ₆ F ₂ were $\sigma_p = 3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 110°C and E = 0.42 eV, respectively.
(NH ₄) ₂ O(Ga ₂ O ₃) ₁₁ (H ₂ O) _{1.25}	C	<500°C		67, 68	This gallate losses water at 180°C and ammonia at 230°C to form a hydroxide which decomposes at 460°C to Ga ₂ O ₃ . Protonic transference number was close to 1 (especially at temperatures above 100°C). Irregular conductivity dependence on temperature was observed with two characteristic maxima, $\sigma_p = 5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at about 200°C (before NH ₃ liberation), $\sigma_p = 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at about 450°C (before final dehydration) and a rapid drop in protonic conductivity above 460°C. Many problems were connected with fabrication of this electrolyte.

Table 1, Part 9. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5 \text{H}_2\text{O}$	C	<200°C (cond.)	69	Dehydration occurred with increasing temperatures: first, second, and third H_2O molecules were evolved in the temperature ranges 110° to 180°C, 180° to 220°C, and 220° to 270°C, respectively. Total conductivity varied within the 10^{-5} to 10^{-6} ohm $^{-1}$ cm $^{-1}$ interval in the temperature range 35° to 200°C. Both O_2 and H_2 evolutions were observed due to mixed-type conductivity. Transference numbers 0.80 and 0.14 were found for proton and oxygen ion, respectively.
Organic Acids	--	<100°C	10	Melts usually below 100°C. Low conductivity values were reported ($\sigma_p \approx 10^{-9}$ to 10^{-10} ohm $^{-1}$ cm $^{-1}$).
$\text{TiH}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	--	<300°C	40,70	Significant increase in activation energy was found after dehydration of two water molecules ($E = 2$ kcal mol $^{-1}$ at -10°C, $E = 13.9$ kcal mol $^{-1}$ at 300°C). Conductivity of $\text{TiH}_2(\text{PO}_4)_2$ was measured at 250°C ($\sigma = 1.2 \times 10^{-6}$ ohm $^{-1}$ cm $^{-1}$) and 300°C ($\sigma = 4 \times 10^{-6}$ ohm $^{-1}$ cm $^{-1}$).
$\text{CeH}_2(\text{PO}_4)_2 \cdot 2 \text{H}_2\text{O}$	--	<300°C	40,70	$\sigma = 10^{-6}$ ohm $^{-1}$ cm $^{-1}$ at 250°C.

Table 1, Part 10. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
a-ZrH ₂ (PO ₄) ₂ · H ₂ O (p-ZP)	B	1000°C	40, 71, 72	Thermal decomposition proceeded in accordance with the sequence (interlayer distance in brackets): ZrH ₂ PO ₄ · H ₂ O (0.756 nm) $\xrightarrow{110^{\circ}\text{C}}$ ZrH ₂ PO ₄ (0.741 nm) $\xrightarrow{220^{\circ}\text{C}}$ ZrH ₂ PO ₄ (0.680 nm) $\xrightarrow{450^{\circ} \text{ to } 550^{\circ}\text{C}}$ ZrP ₂ O ₇ (0.610 nm) $\xrightarrow{800^{\circ} \text{ to } 1000^{\circ}\text{C}}$ ZrP ₂ O ₇

Conductivity was found to be dependent on the direction of the applied electric field as well as the method of preparation ($\sigma = 3 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ in crystal for electric field applied perpendicular to pellicles, $\sigma = 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ in crystal and electric field applied parallel to the pellicles, $\sigma = 5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ in p-ZP prepared from microcrystalline powder -- all data at 300°C). Activation energy of about 50 kJ mol⁻¹ was found (calculated from the conductivity plot presented by Alberti et al.⁷²). Stabilization of conductivity values after a few heating cycles was found.

Table 1, Part 11. CONDUCTIVITY DATA OF SOME SSPC

Compound	Type*	Temperature Range Investigated	Refs.	Remarks
ZrO ₂ · nH ₂ O	B	1000°C	73	$\sigma = 0.2 \text{ to } 1.0 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ in ZrO ₂ · 1.75 H ₂ O (dependent on the method of structure preparation) at 27°C (E = 0.35 eV). Above 40°C structure began to decompose. Complete dehydration occurred at 650°C.
SnO ₂ · nH ₂ O	B			$\sigma = 4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ in SnO ₂ · 2H ₂ O at 27°C. Complete dehydration occurred at 1000°C. Decomposition of antimonous acid proceeded as:
SbO ₂ · nH ₂ O				$3.0 (\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}) \xrightarrow{1000^\circ\text{C}}$
				$2 \text{ Sb}_3\text{O}_6\text{OH} + (3x-1) \text{ H}_2\text{O} + \text{O}_2$
				with x in the range 3 to 4. Conductivity of Sb ₂ O ₅ · 4H ₂ O was found to be similar to that of SnO ₂ · 2H ₂ O at room temperatures.
Cs ₆ [H ₂ (W ₃ O ₁₀) ₄]	--	<900°C	161	$\sigma_T = 6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C. Decomposition starts at 293°C. Hydrated at lower temperatures.
Na ₄ H ₂ [H ₂ (W ₃ O ₁₀) ₄]	--	<800°C	161	$\sigma_T = 4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C (hydrated form). Begins to decompose at 315°C. Loss of second molecule of constitutional water probably at 410°C.
H ₃ [P(W ₃ O ₁₀) ₄]	--	--	161	$\sigma_T = 2 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C (hydrated form).
H ₄ [Si(W ₃ O ₁₀) ₄]	--	<600°C	161-162	$\sigma_T = 3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C (hydrated form). Decomposes in the temperature range 435° to 525°C.

* Type of conductivity data dependence on temperature: A: $\text{Ln}(\sigma) = \text{Ln}(\sigma_0) - E/RT$;
 B: $\text{Ln}(\sigma_T)_0 = \text{Ln}(\sigma_T)_0 - E/RT$; C: irregular dependence.

Most of the protonic conductors, especially at lower temperatures, have hydrogen as a major constituent, but protonic migration occurs also in an oxide host. The KTaO_3 crystal, having the perovskite structure, is a typical example. Infrared measurements show a sharp OH^- absorption band that indicates introduction of a proton into this material from a hydrogen containing atmosphere.⁷⁵ Similar results were obtained by Lee and Nowick⁷⁶ who doped KTaO_3 crystals with Cu^{2+} , Fe^{3+} , and Ni^{3+} ions and introduced protons into doped structure by heating in water vapor at 900°C . The EMF of the cell:

was found to be reversible with changes in temperature. Protonic transference number, t_p , from EMF measurements indicated almost completely protonic conductivity ($t_p = 0.98$ at 517°C , $t_p = 0.97$ at 568°C , and $t_p = 0.93$ at 626°C). Activation energies in the expression:

$$\sigma T = A \exp(-E_a/kT) \quad (5)$$

were found in the range 1 to 1.1 eV for all dopants. Proton conductivity increased in the sequence:

$$\sigma(\text{KTaO}_3:\text{Fe}^{3+}) > \sigma(\text{KTaO}_3:\text{Cu}^{2+}) > \sigma(\text{KTaO}_3:\text{Ni}^{3+}) \quad (6)$$

at the same intensity of the OH^- absorption band (the same proton concentration) but the conductivity level did not exceed $2 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 350°C for the doped ion concentrations used. Measurements were carried out only for temperatures below 450°C .

An estimation of total conductivity at 800°C may be made by assuming the same activation energy, E_a , as in the temperature region below 450°C and gives

$$\sigma(\text{KTaO}_3:\text{Fe}^{3+}) = 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \quad (7)$$

But one may expect much lower proton transference number values at higher temperatures. An increase in conductivity may also be possible by increasing the Fe^{3+} ions concentration.

2.2. Current Status of the Medium Temperature SSPC Development

Considerable development of SSPC in the 400° to 1000°C temperature range has occurred in the last decade, especially in Japan in the Department of Environmental Chemistry and Technology group at Tottori University. During 1980 and 1981, Iwahara *et al.*^{15,77} demonstrated a relatively high ionic conductivity of some SrCeO₃-based oxides and confirmed their proton conductivity. Specimens were prepared as a thin sintered disk (0.05 cm thick) and tested in a cell of the type:

with dry and wet air, O₂ and H₂ as gases 1 and 2. Undoped SrCeO₃ showed unstable EMF in all cases, but doped ceramics of the type SrCe_{1-x}M_xO_{3-α} (M = Yb, Mg, Y, Ln, Znb, Nd, Sm; x = 0.05-0.1) showed peculiar EMF's that could be explained only in terms of mixed protonic-electronic conductivity (index α describes number of oxygen deficiencies per perovskite-type oxide unit cell). The highest conductivities have been found for SrCe_{0.95}Yb_{0.05}O_{3-α}, σ = 10⁻³ ohm⁻¹ cm⁻¹ at 600°C and σ = 10⁻² ohm⁻¹ cm⁻¹ at 1000°C in a hydrogen atmosphere, with protonic transference number, t_p, equal to 0.84 at 1000°C. Higher proton transference numbers were observed at lower temperatures.

SrCeO₃-based proton conductors were intensively investigated as an electrolyte in a steam concentration cell and for steam electrolysis,^{11,13,17,20,75} as a galvanic cell type humidity sensor,¹⁸ as a solid electrolyte fuel cell,^{2-4,9} as a hydrogen concentration cell,⁴ and for extraction of hydrogen gas.²⁰ Although of lower total conductivity than BaCe_{0.95}Yb_{0.05}O_{3-α} (See Figure 3), SrCe_{0.95}Y_{0.05}O_{3-α} has been used in all the above applications because of a higher proton transference number in the temperature range 800° to 900°C.

The comprehensive set of conductivities and proton transference numbers was presented by Uchida *et al.*⁷⁸ at different gaseous atmospheres. Within the O₂, H₂O containing atmosphere:

- Protonic conductivity increases as P_{H₂O} increases and is generally independent of O₂ partial pressure (at constant P_{H₂O})

$$\sigma_p(P_{O_2}, P_{H_2O}) = P_{H_2O}^{0.5} \quad (8)$$

- Total conductivity increases when P_{O₂} increases or P_{H₂O} decreases.

Figure 3. COMPARISON OF SPECIFIC IONIC CONDUCTIVITIES FOR THE SELECTED OXIDE ION AND PROTONIC CONDUCTORS

An interesting theoretical and experimental work was published in 1987 by A. Mitsui et al.⁷⁹ from Tokyo University. It was suggested that a static lattice stimulation model is applicable for the estimation of activation energy of proton conductivity. For CaHfO_3 , BaZrO_3 , SrCeO_3 , and BaCeO_3 crystal lattices, it was calculated that a total energy distribution for proton interactions with the crystal lattice where total energy is the sum of Coulombic energy and overlap repulsion energy. A. Mitsui et al.⁷⁹ determined a three-dimensional conduction path for the proton by connecting the lowest energy points. A difference between the maximum and minimum energy along the path of minimum energies was taken as an activation energy, E_a , for migration of the proton within the lattice. The calculated activation energies were larger than the observed values, but showed a similar dependence on lattice parameter (increase in activation energy with increase in lattice parameter a). The authors are of the opinion that differences in the calculated activation energy are only due to omission of other energy terms such as induced dipole-dipole interaction energy, monopole-dipole interaction energy as well as relaxation of the lattice introduced by Yb_2O_3 doping. Measurements of total conductivity showed the sequence:

$$\sigma(\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}) > \sigma(\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}) > \sigma(\text{BaZr}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}) > \sigma(\text{CaHf}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}) \quad (9)$$

within the temperature range of 400° to 800°C, and confirmed nearly equal proton transference numbers ($t_p = 0.8$ to 0.85) for $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ and $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ below 600°C in wet air.⁷⁸

Recent data published by Iwahara et al.¹⁶³ indicate a high proton conductivity for $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\alpha}$ perovskite oxide. Measured values for proton conductivity, $0.038 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1000°C and $0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 750°C, are the highest reported up to the present time in this temperature range. A high proton transference number of about 0.95 was observed in this material at a hydrogen partial pressure of 1 atmosphere. A fuel cell was assembled at Tottori using this electrolyte and noble metal electrodes. The cell incorporated a 0.56 mm thick electrolyte. Total cell resistances of about 5 ohm were measured at 800°C with hydrogen as the fuel and air as the oxidant. Linearity of the current-voltage characteristics was observed over the full

range of currents measured. However, water was detected on both sides of the fuel cell, indicating either simultaneous oxide ion conduction or a leak in the system.

Some new data have been published addressing proton conductivity of the strontium ytterbiate cerate, $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$, the classic high-temperature proton conductor. Bonanos *et al.*⁸⁰ reported mixed oxide ion/electronic conductivity in an oxygen rich atmosphere. The ionic transference numbers of 0.97 and 0.76 at 600°C were found in air and oxygen, respectively. It was postulated that ionic conduction in the perovskites is dominated by oxide ion transport, and that any protonic transport occurring in a hydrogen-rich atmosphere is coupled to oxide ion transport. These results contradict the observations by Iwahara *et al.*⁸¹ of a null response of the cell for an oxygen concentration cell with dry gases. Therefore, the question of the conduction mechanism in this classic compound remains open (See Figure 4).

A review of proton conductivity and its applications in the SrCeO_3 -based compounds was published by Iwahara.⁸² Two reaction mechanisms were indicated as a possible source of proton formation --

or

where h = hole, V_O = oxygen vacancy, O_O = oxide ion, H^+ = proton. Knowledge of the reaction mechanism under a given set of conditions is crucial for the design of devices for proton conducting applications.

Measurements of the bulk conductivity of Fe^{3+} doped KTaO_3 and Yb^{3+} doped SrCeO_3 and BaCeO_3 were presented by Scherban *et al.*⁸³ Two correlations were postulated. The activation energy for bulk proton conduction was found to decrease as the oxygen-oxygen distance increases and also as the dielectric constant decreases.

The following conclusions can be drawn from the paper published by Iwahara's group, regarding perovskite oxide based proton conductors:

H. Iwahara (1983)⁸²
(Tottori University, Japan)

- Partial substitution of Yb^{3+} for Ce^{4+} ions on the 'B' site give rise to oxide ion vacancies (V_O)

- Oxide ion vacancies react with gaseous oxygen to produce holes in the conduction band

- Protons are produced by the subsequent reaction of these holes with water vapor or hydrogen

- Protons are mobile and pass through the solid.

N. Bonanos et al. (1988)
(British Petroleum Research Center, UK)

- Typical oxide ion conduction take place in this compound
- Hydrogen transport is by linkage to an oxide ion, and hydrogen transport is in fact hydroxide ion transport
- This is contradictory with the model of proton conduction by Iwahara
- Both theories have a partial confirmation by experimental data.

Figure 4. FUNDAMENTAL ASSUMPTIONS OF THE PROTON MECHANISMS IN THE PEROVSKITE TYPE OXIDES AS PROPOSED BY BONANOS ET AL.⁸⁰ AND IWAHARA⁸¹

- Short circuit currents of more than 170 mA/cm² (at 900°C) have been reported for a SrCe_{0.95}Yb_{0.05}O₃ electrolyte based fuel cell operating on a mixture of methanol and water as a fuel.
- With the same fuel, and air as an oxidant, short circuit current was 400 mA/cm² for a BaCe_{0.90}Nd_{0.10}O₃ electrolyte.
- Results from the SrCe_{0.95}Yb_{0.05}O₃ electrolyte based fuel cell reported on in this paper are consistent with the results obtained in IGT laboratories.
- A BaCeO₃ electrolyte was found to have some oxide ion conductivity in addition to the majority proton conductivity in the high-temperature region. No information regarding minor oxide ion conduction of SrCe_{0.95}Yb_{0.05}O₃ electrolyte was reported, however.
- Methane mixed with water vapor (CH₄+H₂O) was also used as a fuel with SrCe_{0.95}Yb_{0.05}O₃ electrolyte. Short circuit current of 140 mA/cm² was reported in this case.

A paper coauthored by H. Iwahara, H. Uchida, and K. Morimoto from Tottori University (Japan) presented results of experiments with a BaCe_{0.9}Nd_{0.1}O_{3-α} electrolyte.⁸⁴ Short circuit current densities (SCC) in the range of 250 to 300 mA/cm² were reported at 800°C. Maximum current of 650 mA/cm² was reached with Pt porous electrodes at 1000°C. Water vapor was produced in both anode and cathode compartments. Based on the water vapor evolution rate, proton conduction was estimated to be 80% and oxide ion conduction was estimated to be 20% of the total ionic conduction at 800°C. The ionic transport number was about 0.9 at 1000°C. No conduction mechanism was suggested in this paper. Several cell/fuel combinations were tested including a methanol fuel, a methane fuel, and a fuel cell using a porous nickel anode. Results presented in the paper show very low electrode polarization, which is encouraging even though there were indications of minor conduction by species other than H⁺. Stable performance was achieved operating the cell with methanol as a fuel at 900° to 1000°C. Because of the lower hydrogen concentration used, this cell was operated at slightly higher polarization (SCC was less than 500 mA/cm² at 1000°C). When methane was used as a fuel, the addition of water vapor to the methane, a commonly used procedure, was found to give stable cell performance. The use of nickel as a fuel electrode decreased the cell performance by 15% to 20% over that observed with platinum. Experiments with oxide electrodes were mentioned, but no further information was given in the paper.

2.3. Electrodes for Moderate Temperature (SSPC) Fuel Cell

Many requirements could be listed for acceptable electrodes for SSPC fuel cell. A few of them are indicated below:

- The porous structure of the electrodes as well as the electrode/electrolyte interface must be physically and chemically stable.
- Electrical conductivity of the electrode materials should be high to prevent resistance polarization (electronic).
- The product of the electrochemically active internal surface area and the kinetic rate constant should be high to prevent activation polarization.
- Ease of access of gaseous reagents and the release of gaseous products should be insured to minimize concentration polarization.
- A relatively high protonic conductivity of the cathode is useful to insure proton accessibility and to avoid ionic resistance polarization.
- The electrode materials must have very low vapor pressure at the operating temperature to prevent their evaporation.

A limited number of studies has been done related to electrodes for SSPC fuel cell at high temperatures.

Anode. Porous platinum metal anodes have been commonly used.^{2-4,11,20} The platinum paste was smeared on the face of the specimen electrolyte, for example ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$), and fired at 1000°C in open air for 1 hour.³ Platinum paste was prepared by suspending a fine platinum powder in n-butyl acetate. Polarization of the anode (fuel composition: $P_{\text{H}_2} = 0.975$ atm, $P_{\text{H}_2\text{O}} = 0.025$ atm) was negligibly small in the temperature range of 800° to 1000°C and the anodic reaction was considered to occur reversibly.³ Nickel was also adapted as anode material² in place of expensive platinum. A paste of nickel formate was smeared on to a $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\alpha}$ ceramic disc. After baking at 900°C for 1 hour in air, the nickel oxide was reduced to porous metallic nickel. The nickel electrode also showed negligible polarization at 1000°C. Current densities less than 200 mA/cm² were examined, but problems were reported with contact resistance. Anodic polarization increases at temperatures below 1000°C ($\eta_a = 40$ to 50 mV at 60 mA/cm² and 800°C) and appears to be more significant at still lower temperatures. Also, cobalt was examined as an anode and was rejected due to large polarization and high contact resistance.² Data on anode operation at temperatures lower than 800°C, at low hydrogen partial pressure, and high current densities were not

reported in the literature, nor was the anodic reaction mechanism addressed. It should be noted that problems of Pt evaporation and material stability arise in the 900° to 1000°C temperature range.⁸⁵

Cathode. A porous platinum electrode has also been used as a cathode in the fuel cell:^{2,4} H_2 (or C_2H_6), Pt/SrCe_{0.95}Y_{0.05}O_{3-α}/Pt, air. Cathode polarization measurements gave a very high value of above 400 mV at 100 mA/cm² and 800°C. Again, electrode polarization increases significantly with decreasing temperature from 900° to 800°C. Based on previous studies of oxide electrodes for oxide ion fuel cells,⁸⁶⁻⁸⁸ LaCrO₃-based perovskite oxide was rejected because of chemical reaction with the electrolyte, Sn-doped In₂O₃ was rejected because of large polarization and high contact resistance. Only porous La_{0.4}Ca_{0.6}CoO_{3-α} and La_{0.4}Sr_{0.6}CoO_{3-α} exhibited comparatively good characteristics. Cathodic polarizations of about 150 mV at 1000°C and about 270 mV at 800°C were measured at 100 mA/cm² in wet air. However, deterioration of electrode characteristics occurred after 8 hours at 900°C.

The papers discussed above cover all the up-to-date studies of electrodes for SSFC fuel cell at higher temperatures, however, it is useful to review a few of the works related to oxide ion fuel cell cathodes.⁸⁵⁻⁹⁷ Werkerk et al.⁹¹ compared polarization behavior of Pt-sputtered (0.75 μm) and Pt-gauze electrodes in the temperature region 500° to 780°C. They found that for the same electrode morphology, the electrode process is strongly influenced by the nature of the electrolyte. The resistance of a Pt-sputtered cathode was 50 times smaller than a Pt-gauze cathode for ZrO₂-ScO₂ electrolyte, but the same activation energy and limiting current density were observed. The authors concluded that the reaction area is correlated with the length of the three-phase line (gas, Pt, and electrolyte) and not with the two-phase electrolyte/Pt contact area. Mizusaki et al.^{92,93} recently published results of their studies on reaction kinetics at a Pt, O₂(g)/stabilized zirconia system in a wide range of oxygen pressures (10⁻⁴ atm to 1 atm) and temperatures (400° to 800°C). They showed that dissociative adsorption of oxygen molecules on the Pt surface is usually the rate determining step at temperatures below 500°C, as opposed to the temperature region above 600°C where surface diffusion of oxygen atoms on the Pt surface and into the Pt/zirconia contact is the rate limiting step.

Recent cathode investigations by Yamamoto et al.⁸⁵ reported excellent results using perovskite type oxides of high electroreduction activity and relatively high electronic conductivity (10^1 to $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$) when applied using thin film techniques. LaCoO_3 and $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ ($\text{M} = \text{Cr, Mn, Fe, Co}$) films were sputtered onto the YSZ electrolyte under an argon pressure of 1×10^{-2} Torr at a deposition rate of about $0.5 \text{ }\mu\text{m/hr}$. Polarization experiments were carried out at 800°C . A cathode overpotential below 10 mV was measured at 100 mA/cm^2 as a result of thickness optimization of the sputtered LaCoO_3 film. A minimum in the overpotential was observed for a 2 micron thick cathode with pores having an average diameter of about 1 micron. A strong overpotential dependence on annealing temperature (800° to 1000°C) and annealing period (0 to 12 hr) indicates the importance of cathode preparation on its activity. Other perovskite oxides mentioned above were also tested, however, none were as good as LaCoO_3 . A strontium doped lanthanum cobaltite, $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$, was also evaluated as a cathode and exhibited a linear dependence of cathode overpotential on the log of the current density up to 400 mA/cm^2 . The performance of this material was good with an overpotential of only 40 mV at 100 mA/cm^2 . This cathode material is similar to a material used by Iwahara et al.² in their SSPC fuel cell studies, $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$. However, this material used as a SSPC cathode exhibited an overpotential six times that reported above for the SOFC experiment. One possible explanation for this surprising comparison is as follows: Nakamura et al.⁹⁸ discussed a source of oxygen vacancies and Co^{4+} ions of abnormal valence in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. When Sr^{2+} is partially substituted for La^{3+} , the charge is compensated by the oxidation of Co^{3+} to Co^{4+} and/or the formation of oxygen vacancies as is formulated by:

Electronic conduction in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is due to electrons hopping between Co^{3+} and Co^{4+} . Therefore, the electronic conductivity is very dependent on the amount of the couples $\text{Co}^{3+}/\text{Co}^{4+}$. These couples together with the concentration of oxygen vacancies strongly influence chemisorption and

diffusion of oxygen.⁸⁵ The conductivity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ was reported by Buren *et al.*⁹⁴ to be at about $10 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 800°C , and an even lower conductivity would be expected for $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$. On the other hand, Yamamoto *et al.*⁸⁵ observed electrical conductivity above $300 \text{ ohm}^{-1} \text{ cm}^{-1}$ in $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ and near $800 \text{ ohm}^{-1} \text{ cm}^{-1}$ in pure LaCoO_3 .

Surface diffusion of oxygen on the electrode internal surface^{95,96} appears to be the rate determining step for oxygen electroreduction in $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ -type electrodes as suggested by Yamamoto *et al.*⁸⁵ but a quantitative description of this process seems to be difficult because of the lack of basic research in this field, especially for electrodes with complex pore structures.⁹⁷

2.4. Basic Material and Measurement Techniques Applicable for SSPC Development

Many experimental techniques used in the study of SSPC fuel cells are listed in Table 2. Electric techniques as well as thin film techniques are discussed in more detail below.

2.4.1. EMF Measurements

EMF measurements of a cell operating on different gases such as wet and dry air, oxygen, or hydrogen is the simplest method for determining the conductive species. The following equation applies to the EMF of a cell with mixed protonic-electronic electrolyte, and different chemical potential, μ , for hydrogen, $\text{H}_2^{(1)}$ and $\text{H}_2^{(2)}$, at each electrode.

$$E = \frac{1}{2F} \int_{\mu_{\text{H}_2}^{(1)}}^{\mu_{\text{H}_2}^{(2)}} t_p \partial \mu_{\text{H}_2} \quad (15)$$

Substituting hydrogen partial pressure for chemical activity and assuming that the proton transference number, t_p , is independent of electrochemical potential, thus, the following simplified expression --

$$E = t_p \frac{RT}{2F} \ln \frac{P_{\text{H}_2}^{(2)}}{P_{\text{H}_2}^{(1)}} \quad (16)$$

Table 2. SOME TECHNIQUES APPLICABLE FOR SSPC DEVELOPMENT

Technique	Applications	References
MEASUREMENT TECHNIQUES		
EMF	Recognition of conductive species, transference number	99-102
D.C. Polarization	Partial ionic and electronic conductivities, transference number	99,103-105
A.C. Impedance Spectroscopy	Partial ionic and electronic conductivities, transference number, interfacial and grain boundary phenomena	93,100,105-110
Coulometric Studies Coulometric Titration	Determination of transference number of ionic species. Recognition of conductive ionic species	69,111,112
NMR (Nuclear Magnetic Response)	Direct investigation of proton motion. Determination of diffusion coefficient of the conductive species Estimation of protonic conductivity using Nernst-Einstein equation. Conduction mechanism.	31-36,46
IR (Infra-red Spectroscopy)	Localization of conductive species on the molecular level. Determination of relative proton concentration. Conduction mechanism.	13
X-ray	Determination of stoichiometry and structure of the investigated material.	80,113

Table 2, Cont. SOME TECHNIQUES APPLICABLE FOR SSPC DEVELOPMENT

Technique	Applications	References
MATERIAL TECHNIQUES		
TGA, DTA (Thermal Analysis)	Determination of phase changes, dehydration processes, composition changes and their reversibility.	52,69,105
SEM, HRTEM (Electron Microscopy)	Surface structure and properties of investigated material.	8,114
FAIE (Field Assisted Ion Exchange)	Many polycrystalline proton conductors have been obtained by this method. Mobile ions of the solid substrate (e.g., K^+ , Na^+ ...) are removed into surrounding liquid electrolyte by electric field. On the other side, H_3O^+ (or other ions) are introduced into the solid from liquid electrolyte:	61,62
	$H_3O(liqu.el.) \rightarrow H_3O^{+} X^{-} (solid)T$ $Na^{+} X(solid) \rightarrow Na^{+} (liqu.el.)$	
Intercalation	Intercalation is a general name for introducing atoms between the layers of many layered materials. Materials such as TiO_2 constitutes a host lattice that enables intercalation.	115-117
Thin Film Techniques	D.C. and r.f. sputtering, chemical vapor deposition (CVD), electrochemical vapor deposition (EVD) and other methods are useful for electrolyte or electrode fabrication of the 1-30 μm thickness.	85,118-120

where superscripts (1) and (2) denote different hydrogen concentration for a fully protonic conductor, $t_p = 1$. Generally, ionic transport number cannot be taken in front of the integral sign but sometimes this is done and in this way the calculated transference number, t_p , represents a kind of average transport number.^{99,101} One should remember, however, that t_p is really a function of the chemical potential of hydrogen and, at lower transference numbers, calculating t_p from Equation 16 has a limited meaning and may lead to confusion or erroneous results.

Another way to calculate proton transference number using EMF measurements is based on the following equation:^{99,100-102}

$$t_p(\mu_{H_2}^{(2)}) = 2F \left[\frac{\partial E(\mu_{H_2}^{(1)}, \mu_{H_2}^{(2)})}{\partial \mu_{H_2}} \right] \mu_{H_2}^{(2)} \quad (17)$$

obtained by differentiation of Equation 17 with respect to the upper limit of integration.

2.4.2. Alternating Current Measurements

Alternating current (ac) measurements provide a powerful tool for the determination of ionic transport properties and interfacial reaction mechanisms. A number of review papers have been published recently on various aspects of this technique,¹⁰⁶⁻¹⁰⁸ but only a little data are available for protonic conductors,^{105,109,110} especially at higher temperatures. For the ideal case, finite R and C elements (resistance and capacitance), the impedance diagram consist of a combination of semicircles and vertical lines. In reality, however, the picture becomes more complicated. The variations of each arc and the variations of the intersection of each arc with the real axis with temperature, applied voltage, partial pressure of gases, electrode surface, etc. allow possible phenomenon to be assigned to each arc.

A typical application of this approach was presented by Goge *et al.*¹⁰¹ for ytterbia and samaria stabilized zirconia, investigated in the temperature range of 400° to 800°C. Frequencies in the range of 10^2 to 10^6 Hz were applied. On the basis of equivalent circuit analysis, they were able to determine basic system parameters and calculate ionic transport numbers.

It was shown by various authors that EMF measurements by themselves may lead to transference numbers which sometimes differs significantly from the "true" transference number.^{121,122}

2.4.3. Direct Current Measurements

Direct current (d-c) measurements are the method of choice for separation of ionic and electronic contributions to the conductivity. Electron-blocking or ion-blocking electrodes are used to separate the respective conductivities. For example, a mixed oxide ion/electronic conductor electrolyte operating between two identical electrodes has the serious disadvantage that complete reversibility of electrodes can seldom be achieved with direct current¹⁰⁴ and total conductivity cannot be determined reliably.

However, the electronic conductivity can be measured using a galvanic cell like the following:⁹⁹

When Pt' electrode is polarized anodically, only electrons can flow through the cell, since oxide ions cannot be formed on the nitrogen side of the cell. In this case, the nitrogen turns the Pt'' electrode into a blocking electrode for oxide ions. Partial electronic conductivity, σ_e , as a function of oxygen partial pressure can be determined by this method:

$$\sigma_e (\mu'_{O_2}) = -4F \ln \left(\frac{\partial i}{\partial \mu_{O_2}} \right) \mu'_{O_2} \quad (18)$$

$$\mu_{O_2} = \mu_{O_2}^0 + RT \ln P_{O_2} \quad (19)$$

The same method applies for mixed protonic/electronic conductors.

The alternative case of an electron-blocking electrode can be achieved, for example, by insertion of an ion-only conductive membrane between one electrode and the mixed conductor. A nafion membrane was used by Greaves et al.¹⁰⁵ to measure the protonic conductivity of the mixed protonic/electronic conductor, Ni_2O_3H , at 20°C. However, at higher temperatures (400° to 1000°C) such an ion-only reference does not exist.

2.4.4. Thin Film Techniques

Because of relatively low specific conductivities of the available SSPC, thin film techniques are particularly useful methods of electrolyte and cathode fabrication. Many of the same techniques used with oxide ion conductive electrolytes are applicable for SSPC electrolytes.

2.4.4.1. Chemical Vapor Deposition (CVD)

This is a technique that is widely used in the fabrication of surface coatings for high-temperature application. In this technique, solid product is formed on the support by the reaction of gaseous reactants. However, limitation on the control of thickness is one of a few problems encountered when using CVD.¹²³ Significant improvement in CVD of thin layers of oxide was made by Isenberg.^{118,119} The process employs metal chlorides (for example, mixture of $ZrCl_4$ and YCl_3) in quantities necessary to form the required oxide composition (for example, $ZrO_2-Y_2O_3$). A steam/hydrogen mixture is supplied through a porous support structure. In the first step, oxide is deposited by direct CVD, sealing the outer pores of the support. In the second step, the reaction proceeds via an electrochemical reaction using the first layer as an electrolyte. The major advantage of electrochemical vapor deposition (EVD) is that pores are completely sealed, preventing leakage of gas across the electrolyte. A 30-micron thick electrolyte layer has been obtained by using this method.¹²⁴

2.4.4.2. Sputtering.

The sputtering technique is another method applicable for thin film deposition.¹²⁵⁻¹²⁸ In this technique, a substrate target of the required composition is used as a cathode. Argon is usually used to form a plasma in d-c sputtering. The substrate is sputtered onto the support with a deposition rate at about 0.5 μ/h depending upon the applied power. Higher rates can be achieved with r.f. sputtering. A 1 to 3 microns thick porous cathode has been obtained recently⁸⁵ by r.f. sputtering.

2.4.4.3. Vacuum Vaporization

A 5 micrometer thick zirconia-yttria stabilized film ($ZrO_2-Y_2O_3$) was prepared by oxidizing a composite film of metal formed by vapor deposition.¹²⁰ Composite Zr-Y layers were obtained by vacuum evaporation of metals onto a nickel substrate using an electron gun. The total thickness of the cell was

50 microns and no apparent damage was found after heat cycles between room temperature and 650°C.

2.5. Modeling and Optimization Studies

Little modeling and optimization research have been done in the field of SSPC fuel cell, particularly at higher temperatures. A recent paper presented by Canaday *et al.*¹²⁹ describes the basic sources of polarization and their implications for cell voltage, power density, and cell design at a temperature of 300°C.

At temperatures of about 800°C, cathodic polarization and ohmic losses are the basic causes of cell polarization.^{2,4} Anodic polarization is also expected to increase considerably below 800°C. In the previous chapters, a few approaches were discussed to improve SSPC fuel cell operation. To improve output, a polarization model of the SSPC fuel cell is necessary. The purpose of the experimental work which follows is improved power density and increased understanding of the SSPC fuel cells.

Understanding of the mechanism of charge transfer through the electrolyte and the electrode reaction mechanism are the basic problems that need to be addressed in order to optimize the electrode configurations and other cell parameters (internal surface, materials, porosity, thickness, contact surface with the electrolyte, temperature, gas composition, etc.). The reaction site at the cathode for the charge transfer process is generally thought to occur at the electrolyte/cathode/gas boundary line for oxide ion conducting cell.^{91-93,129-131} An advanced approach to the problem of electrode reactions in this case was presented by Perfilyev.¹³² However, very little information is available for the case of the proton conducting cell.

3.0. CORRELATION AND OPTIMIZATION STUDIES

3.1. Correlation Studies on Proton Conduction

At present, the low specific conductivity of protonic conductors requires fabrication by thin film techniques in order to achieve electrolyte resistances of practical interest. Optimization of the product $\sigma_p l$ (where l is electrolyte thickness) at reasonable costs seems to be the key for successful application of this technology (See Figure 5). The following requirements constitutes additional constraints on SSPC applications:

- Proton conductivity at least $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at the fuel cell operation temperature
- Proton transference number, t_p , 0.95 or above
- Thermal and chemical stability in the temperature range up to 800°C in both reducing and oxidizing atmospheres and at different water vapor pressures
- Satisfactory mechanical and thermomechanical properties
- Compatibility with electrode materials
- Commercialization capabilities -- relatively low costs of fabrication.

Two groups of materials have been selected as a result of initial literature searches:

1. Perovskite oxides of the type:

where:

α = oxygen deficiency

A = Ca, Sr, Ba,...

oxidation state = II

B = Ce, Zr, Hf, Th,...

oxidation state = IV

M = Y, Yb, Mg, Sc,...

x = 0.01-0.10

2. Hydrogen double phosphates of the general formulas:

where:

X^V = As, Sb

X^{IV} = Si, Ge, Sn, Pb, Ti, Zr, Hf, Ce, Th

X^{III} = Dy, Y, Ho, Er, Tm, Tb, Lu

Figure 5. ISORESISTANCE LINES FOR ELECTROLYTES OF DIFFERENT SPECIFIC CONDUCTIVITY AND THICKNESS (R -Electrolyte Resistance, ohm). ALSO SHOWN ARE SPECIFIC CONDUCTIVITY VALUES FOR SELECTED ELECTROLYTES

- Hydrogen double phosphates were shown to have a layered structure with interlayer protons which are exchangeable with other cations. They are hydrated at lower temperatures. Recently, Minou *et al.*¹³³ tested SbHP₂O₈ (antimony hydrogen phosphate) and reported that the protonic conductivity of this compound is comparable to the protonic conductivity of SrCe_{0.95}Yb_{0.05}O_{3-α} ($\sigma_p = 5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$). Antimony hydrogen phosphate was shown to be stable up to 800°C. Other compounds of a similar type were also found to be protonic conductors (for example, ZrH₂P₂O₈). However, they decomposed at a lower temperatures (400° to 500°C).
- Besides the two groups of compounds above listed, other promising compounds were considered based on analysis of correlations between protonic conductivity, structural, and physicochemical properties of the materials. The HCa₂Nb₃O₁₀ perovskite oxide, for example, seems to have the required structural properties and stability at moderate temperatures but decomposes to CaNbO₂ and Ca₂Nb₂O₇ after heat treatment at 1000°C for 16 hours. This compound can be prepared by ion exchange of KCa₂Nb₃O₁₀ in acid solution.
- A correlation approach was taken from the literature¹³⁴⁻¹³⁶ and applied here for the initial section of materials.

The cubic perovskite type structure with the positioning of "A", "B", and the oxygen atoms is presented in Figure 6. The doping process involves substitution of some B atoms by dopant D atoms. Doping appears to be necessary for proton conduction in the perovskite oxide group.

A selection scheme for candidate materials for use as proton conducting electrolytes is presented in Figure 7.

Correlation of data from the studies of the proton conductivity of doped A^{II}B^{IV}O₃ perovskite oxides indicate a strong dependence of conductivity and proton transference number on elemental composition and the perovskite cell structure. The requirement that the proton conducting electrolyte have a very low electronic conductivity narrows the range of choices to perovskites in which the π band states are completely empty of electrons and, therefore, net electron spin equals zero. It was shown before by Goodenough¹³⁷ that electric and other physical properties of ABO₃ perovskites are determined mainly by the degree of interaction of the d-orbitals of the B cation with the p-orbitals of the neighboring oxygen anion (B-O-B type interaction). The electronic structure of selected candidate B-type elements with a possible oxidation state +4, are presented in Table 3.

Another parameter that apparently has influence on the conductivity is the dimension and type of elementary perovskite unit cell. The length of the

Figure 6. THE PERFECT PEROVSKITE STRUCTURE OF THE ABO₃ TYPE

Figure 7. PROTON CONDUCTION SELECTION SCHEME FOR THE $A^{II}B^{IV}_{1-x}D_xO_3$ TYPE PEROVSKITE OXIDES

Table 3. ELECTRONIC STATES OF CANDIDATE B ELEMENTS AND DOPANTS (D) IN ABO₃ PEROVSKITES (PARTIALLY FILLED ORBITALS INDICATED BY #)

		<u>4s</u>	<u>4p</u>	<u>4d</u>	<u>4f</u>	<u>5s</u>	<u>5p</u>	<u>5d</u>	<u>5f</u>	<u>5g</u>	<u>6s</u>	<u>6p</u>	<u>6d</u>	<u>6f</u>	<u>6g</u>	<u>6h</u>	<u>7s</u>
B	Zr	2	6	#2		2											
B	Ce	2	6	10	#2	2	6				2						
B	Hf	2	6	10	14	2	6	#2			2						
B	Th	2	6	10	14	2	6	10			2	6	#2				2
D*	Zn	2															
D	Y	2	6	#1		2											
D	Yb	2	6	10	14	2	6				2						
D	Ce	2	6	10	#2	2	6				2						
D	Nd	2	6	10	#4	2	6				2						
D	Sm	2	6	10	#6	2	6				2						
D	Dy	2	6	10	#10	2	6				2						
D	Yb	2	6	10	14	2	6				2						

* Dopant (in doped perovskite AB_{1-x}D_xO₃).

edge of a cube having a volume equal to the volume occupied by one molecule in the unit cell, was used for comparison.

$$(a')^3 = \frac{\text{Volume of the Unit Cell}}{\text{Number of Molecules in Unit Cell}} \quad (20)$$

Some perovskite oxides of interest are compared in Table 4. Although the table is not complete, the relation between unit cell volume (or equivalent edge length) and conductivity is apparent.

The only comparative data regarding dopant effects on protonic conductivity in a reducing atmosphere has been published by Iwahara *et al.*¹⁵ who found the following sequence of protonic conductivity levels at T < 900°C:

Further studies are required to clarify correlation between dopant properties, protonic conductivity and proton transference number. The effective ionic radius of dopant is suspected to be an important factor.

An ionic conductor to be used for electrolyte application should possess high protonic conductivity and an electronic conductivity as low as possible. Therefore, the minimum requirement for electronic bandgap can be formulated.

Table 4. EQUIVALENT CELL EDGE, a' , AND PROTONIC CONDUCTIVITY FOR SELECTED PEROVSKITE OXIDES

<u>A = Ca</u>	<u>A = Sr</u>	<u>A = Ba</u>	<u>a', angstroms</u>	<u>σ, mho $\cdot$ cm⁻¹</u>	<u>t_H</u>
CaHfO ₃				$1 \cdot 10^{-5}$	0.4
CaCeO ₃			3.862		
CaZrO ₃			4.008		
	SrHfO ₃		4.069		
	SrZrO ₃		4.101		
		BaZrO ₃	4.192	$1 \cdot 10^{-3}$	0.1
	SrCeO ₃		4.276	$4 \cdot 10^{-3}$	0.5
CaThO ₃			4.370		
		BaCeO ₃	4.397	$10 \cdot 10^{-3}$	0.25
	SrThO ₃		4.420		
		BaThO ₃	4.485		

It was postulated by Heyne¹³⁸ that the electronic bandgap for "good" solid electrolytes is always larger than $T/300$ eV. This value was developed, however, assuming ionic conductivity of $0.01 \text{ ohm} \cdot \text{cm}^{-1}$ and electronic transference number 0.0001. Such a small electronic transference number does not seem to be required for practical applications and a lower electronic bandgap can be accepted. Because the width of the electronic bandgap is related to the color of a compound, it is possible to estimate, in an approximate way, the behavior of the electrolyte based on its color. For example, BaCeO₃ is colorless at room temperature, indicating a bandgap larger than 3 eV. In fact, this electrolyte was found to be the best proton conducting electrolyte up until now in the temperature range of 400° to 800°C. After doping with Nd, a change in color was observed from white to brown indicating a much narrower bandgap, about 1.5 eV. The doped material had a higher, but still acceptable, electronic conductivity.

The above considerations provided a simple and fast method for preliminary proton electrolytes selection. The three electrolytes: BaCeO₃, SrThO₃, and BaThO₃ were initially selected as a host of the dopant. Neodymium

(Nd) was chosen as the dopant based on its electronic properties (See Table 3) as well as previous successful application.

A search of the literature has provided two publications addressing the preparation of BaThO_3 perovskite compound. The first one, by Nakamura¹³⁹ describes preparation of $\text{BaThO}_{3-\alpha}$ samples and also the results of an X-ray diffraction analysis of the powder. A polycrystalline sample of $\text{BaThO}_{3-\alpha}$ was prepared from BaCO_3 and ThO_2 . A stoichiometric mixture of these components was heated in an alumina boat at 1300° to 1350°C for 1 hour in air. The resulting material was ground, pelletized, and reheated at 1400°C for 6 hours in air. Barium thorium oxide has a white color. A second paper by Bauer and Kristen¹⁴⁰ describes the effect of neodymium incorporation into the perovskite $\text{BaThO}_{3-\alpha}$ structure. A similar method of preparation was chosen by these authors. Powders of BaCO_3 , ThO_2 , and Nd_2O_3 were mixed and reacted in air at 1350°C. The reaction time was not indicated, however. Analysis of neodymium incorporation into BaCeO_3 , BaThO_3 , BaPrO_3 , and BaZrO_3 perovskite structures indicated that trivalent neodymium can be incorporated into the perovskite structure only to a certain extent. After the maximum level of Nd is achieved (for example, 30% Nd in BaCeO_3 or 5% Nd in BaPrO_3), the rest of neodymium forms a new compound with barium and oxygen in which the neodymium exists in the trivalent state (BaNd_2O_4). Incorporation of neodymium into perovskite structures as Nd^{III} is always accompanied by a color change, from white to brown in the case of BaThO_3 . Summarizing:

- $\text{Ba}^{\text{II}}\text{Th}_{1-x}\text{Nd}_x^{\text{III}}\text{O}_{3-\alpha}$: a single-phase perovskite is expected for Nd/Ba ratio less than $x = 0.3$.
- A second phase of $\text{Ba}^{\text{II}}\text{Nd}^{\text{III}}\text{O}_4$ having the calcium ferrite structure is formed for higher Nd/Ba ratio.

No information about the existence of the perovskite SrThO_3 structure was found in the literature. In addition, protonic conduction of this compound was predicted to be worse than for BaThO_3 based compound. Therefore, this hypothetical component was not selected for the experimental study.

3.2. Oxide Cathode Optimization for the SSFC Fuel Cell

The electrocatalytic activity of the cathode is a complex function of the catalytic properties of the active material, the electrochemically active internal surface area, the specific electronic and the ionic resistance, etc. A few possible cathode configurations are shown in Figure 8.

Figure 8. CATHODIC REACTION MECHANISMS FOR DIFFERENT CONFIGURATION OF THE ACTIVE PHASE
(See Text)

- a. An electronic conductor, the electrolyte material and a Pt catalyst are all mixed together within the porous cathode structure. Each material constituent plays a separate role in the cathode operation. This configuration was used by Kahil et al.¹⁴¹ at elevated temperatures with MnO_2 (catalyst), acetylene black (electronic conductor), and HUP (protonic conductor).
- b. Here the electronic conductor is also the catalyst. The most common example is a porous platinum cathode. Electrochemically active surface area is probably limited to the three-phase boundary zone (gas/electrolyte/catalyst). This configuration is commonly used at higher temperatures for both SSPC (porous Pt,⁴ porous $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\alpha}$ ²), and solid oxide electrolyte (SOE) fuel cells (LaCoO_3 , $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\alpha}$.⁸⁵)
- c. A mixed protonic-electronic conductor is the only material component of the porous cathode. The two-dimensional active internal surface area is high and does not require high exchange current densities for oxygen electroreduction. This case is only hypothetical at the present time due to a lack of mixed conductors of specified requirements in the temperature range under consideration.
- d. Electronic conductor is mixed with protonic conductor in order to develop a three-phase boundary zone and decrease concentration polarization. Electrocatalytic properties of the type b cathode could be improved in this way.

The ideal cathode material for use with an SSPC fuel cell is a mixed protonic-electronic conductor, which also dissociatively adsorbs oxygen. Which of the four configurations discussed above is the best for a specific application depends on the electrocatalytic and electrical properties of the cathode material and the most likely sources of polarization. A literature review was conducted to identify candidate cathode materials for use with IGT's electrolyte choices.

Mixed protonic-electronic conductivity has been reported for nickel oxide hydroxide, $\text{Ni}_2\text{O}_3\text{H}$, Greaves et al.¹⁰⁵ Electronic conductivity, $\sigma_e = 4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ and protonic conductivity $\sigma_p = 3.3 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ were measured at 20°C. On the base of the reported activation energy, $E_a = 35 \text{ kJ mol}^{-1}$ one could expect protonic conductivity on the order of $2.3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at about 350°C, no data has been reported, however, at temperatures above 20°C. The crystalline phase of $\text{Ni}_2\text{O}_3\text{H}$, obtained by hydrothermal treatment of the amorphous phase was found to be thermally stable only up to 400°C, where decomposition to NiO occurred. Limits of interstitial proton concentrations in NiO, ZnO, CoO, Cu_2O , and TiO_2 were presented,¹⁴² but data on proton conductivity was not included.

The oxygen molecule is paramagnetic and magnetic properties of materials may play an important role in oxygen adsorption and electrocatalysts. In the case of NiO, adsorption and electroreduction of oxygen increases significantly at temperatures higher than the Neel point where the magnetic properties of NiO changes from antiferromagnetic to paramagnetic.¹⁴³⁻¹⁴⁵ Because transition metal oxides have not been applied as cathodes for SSFC fuel cell, data on their adsorption properties and electrical conductivity were collected instead and are presented in Table 5. For practical applications, doping could be considered as a means of improving electrical conductivity (for example, Li-doped NiO or CoO-NiO mixture).

Table 5. ABSORPTION AND ELECTRICAL CONDUCTIVITY DATA FOR SOME TRANSITION METAL AND OTHER SELECTED OXIDES

Oxide	Oxygen Desorbed at 560°C ¹⁴⁶ cm ³ (STP) m ⁻²	Electrical Conductivity, ohm ⁻¹ cm ⁻¹	Ref.
NiO	1.12 X 10 ⁻²	3 X 10 ⁻² (650°C)	147
CuO	1.42 X 10 ⁻¹	0.2-0.3 (700°C)	148
CoO	--	10 (650°C)	147
MnO ₂	6.54 X 10 ⁻²	10 ⁻¹ -10 ²	149
Cr ₂ O ₃	2.13 X 10 ⁻²	1 X 10 ⁻² (750°C)	148
Co ₃ O ₄	3.30 X 10 ⁻²	1 X 10 ⁻² (--)	148
ZnO	2.45 X 10 ⁻⁴	0.47 at P _{O₂} = 10 ⁻⁴ mmHg and 500°C	148
		0.8 X 10 ⁻³ at P _{O₂} = 150 mmHg and 500°C	148

In spite of much data available related to the use of oxides for oxygen electroreduction in liquid electrolyte systems, their usefulness in IGT's case is limited due to the lack of mobile hydroxide ions which are typical for liquid electrolytes.¹⁵⁰ However, there are several gas/solid chemical reactions, which have reaction mechanisms close to that of oxygen electroreduction. The kinetic rates for these reactions could be used for the initial selection of cathode materials. A useful example is an isotopic homomolecular oxygen exchange --

with the adsorption of oxygen, reaction on the surface and product desorption as the three-step mechanism. It has been shown¹⁵¹ that ionized forms of adsorbed oxygen also take part in homomolecular oxygen exchange. Therefore, an analysis of the literature on the kinetics of chemisorption and oxygen exchange on various oxides will help in predicting the electrocatalytic activity of oxides. A series of data related to this problem has been presented by Boreskov et al.¹⁵²⁻¹⁵⁵ for spinel type oxides ($M^{II}M_2^{III}O_4$).

Measurements were made in the temperature range of 250° to 400°C. On the basis of published exchange rate constants and activation energy, it is possible to extrapolate data into a higher temperature range. A few results are presented in Table 6. Kinetic data are presented in the form of exchange current density to make them more relevant to the present discussion. Values in parentheses are extrapolated to high temperatures. Similar, oxygen isotope exchange methods were used recently by Tannhäuser¹⁵⁶ in order to study the interactions at the yttria stabilized zirconia (YSZ)/air interface.

Table 6. KINETIC RATES AND ACTIVATION ENERGY OF OXYGEN EXCHANGE REACTION FOR SOME SPINEL-TYPE OXIDES

Oxide	Activation Energy kJ mol ⁻¹	300°C	Exchange Current Density in A/cm ² ($P_{O_2} = 1.13 \times 10^{-3}$ atm)	
			600°C	800°C
Co ₃ O ₄	67.0	$17. \times 10^{-6}$		
NiCo ₂ O ₄	88.1	1.2×10^{-6}	(0.7×10^{-3})	(0.7×10^{-2})
ZnCo ₂ O ₄	75.3	2.8×10^{-6}	(0.9×10^{-3})	(0.4×10^{-2})
MgCr ₂ O ₄	121.6	6.3×10^{-9}	(4.1×10^{-5})	(0.9×10^{-3})
CdMn ₂ O ₄	117.4	7.7×10^{-8}	(3.7×10^{-4})	(0.7×10^{-2})

Unfortunately, no data on protonic conductivity have been found for the spinel type oxides in Table 6.

Perovskite type oxides constitutes another broad group of oxygen electroreduction catalysts. Investigations by Yamamoto et al.⁸⁵ reported excellent results using a sputtered LaCoO₃ film working as a cathode in YSZ oxide fuel cell. Also, La_{0.7}Sr_{0.3}MeO₃ (Me = Co, Fe, Mn, Cr) were tested, however, but exhibited poor oxygen electroreduction compared to LaCoO₂

especially at higher current densities. An explanation of such behavior was not included. However, in light of other recent papers^{98,157-159} this behavior becomes clearer. Fierro *et al.*¹⁵⁹ has determined the trends for oxygen adsorption at room temperature, hydrocarbons oxidation, and reducibility by hydrogen for a number of perovskites. High catalytic activity should be observed for oxides having paramagnetic or ferromagnetic properties while antiferromagnetic oxides¹⁴³ should exhibit low activity. A high electroreduction activity is expected for the oxides having the σ^* band partially filled with electrons. On the other hand, when the π^* band is partially filled relatively low activity is expected.¹⁴³ Using this rationale, a comparison of different properties of LaMeO_3 and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MeO}_3$ (Me = Co, Fe, Ni, Mn, Cr) has been prepared.

Electronic	$\text{LaCoO}_3 > \text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3 > \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \gg \text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3 >$
Conductivity	$\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$

Oxygen

Electro-	$\text{LaCoO}_3 > \text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3 > \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 = \text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3 \gg$
reduction	$\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$
Activity	

Oxygen

Adsorption	$\text{LaCoO}_3 \approx \text{LaMnO}_3 > \text{LaNiO}_3 \gg \text{LaCrO}_3 > \text{LaFeO}_3$
(Room Temp)	

Hydrocarbon

Oxidation	$\text{LaCoO}_3 > \text{LaNiO}_3 \approx \text{LaMnO}_3 \gg \text{LaCrO}_3 > \text{LaFeO}_3$
Activity	

Reducibility	$\text{LaNiO}_3 > \text{LaCoO}_3 > \text{LaMnO}_3 \gg \text{LaCrO}_3$
by Hydrogen	

Magnetic	LaNiO_3	LaCoO_3	LaMnO_3	LaFeO_3	LaCrO_3
Properties	(para)	(ferro)	(anti-ferro)	(anti-ferro)	(anti-ferro)

Usefulness of such correlations as a tool for selection of cathode materials is apparent from the above table. From the above considerations, LaNiO_3 seems to be a promising material. Some work with Bi doped LaNiO_3 as a cathode for YSZ fuel cell has been reported.¹²⁴

4.0. EXPERIMENTS WITH THE SSPC FUEL CELL

4.1. Fabrication of the Electrolyte Disks

As a result of studies and a literature review, three electrolytes have been selected for the experimental investigation: $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$, $\text{BaTh}_{0.95}\text{Nd}_{0.05}\text{O}_3$, and $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_3$.

Three disks of the strontium oxyttrerbiate cerate $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ were prepared by Basic Volume (England). They were 99% of theoretical density and 99.99% pure as specified by the manufacturer. These protons conducting electrolyte disks were used during the first run of the test apparatus in order to compare measurements to the manufacturers claims and literature data for the purpose of verifying IGT's experimental procedures.

The $\text{BaTh}_{0.95}\text{Nd}_{0.05}\text{O}_3$ compound was prepared in-house by a reaction between respective amounts of barium carbonate, thorium oxide, and neodymium (III) oxide at 1450°C in air. The powder resulting from the reaction has a brown color which is typical for neodymium compounds in the oxidation state IV. However, attempts to fabricate dense electrolyte disk by tape casting and sintering at 1400°C for 6 hours in air failed. The tape cast disk was too irregular to use as an electrolyte. Therefore, another approach was taken and two $\text{BaTh}_{0.95}\text{Nd}_{0.05}\text{O}_3$ disk, 1 inch in diameter, were formed by cold pressing under 1900 Kg/cm² pressure. These disks were placed in the furnace, heated up to 1000°C in 6 hours, kept in the furnace overnight at this temperature and then cooled. Samples were found to have many cracks, indicating that a more careful heating procedure was required. Preparation of $\text{BaTh}_{0.95}\text{Nd}_{0.05}\text{O}_3$ electrolyte disks was then repeated using a modified heating/cooling procedure, but not much improvement was achieved. Hot-pressing approach was tried and powder sample was sent for custom hot pressing.

Barium-thorium samples were pressed at up to 21 mPa at 1600° and 1750°C. Densities of 80% and 90% of theoretical density respectively were obtained. Surprisingly, material hot pressed at higher temperature broke down into a powder, while lower density material broke into chunks several millimeters across (See Figure 9). A possible explanation would be the existence of a phase transition within the temperature range 1600° to 1750°C presumably accompanied by a significant volume change. The fracturing of the disks to form a powder probably occurred during the cooling process. Confirmation of a

Figure 9. HOT-PRESSED BORIUM-THORIUM BASED SAMPLES AFTER
HOT PRESSING AT 1600°C (Left) AND 1750°C (Right)

phase change in this temperature range was not possible. If a phase transition does occur in this temperature range then the sintering temperature cannot exceed 1600°C. It was not possible during the course of this work to fabricate a sample of barium thorium oxide suitable for testing as an SSPC.

$\text{BaCe}_{1-x}\text{Nd}_x\text{O}_3$ was selected as the next candidate proton conductor to be fabricated. Very good proton conductivity and proton transference number were reported by Iwahara when $x = 0.05$ and $x = 0.10$. However, no data were reported in the literature concerning the ionic conductivity of this material with higher neodymium content ($x > 0.10$). As was discussed previously, neodymium can substitute for cerium up to $x = 0.30$. Excess neodymium over this 30% limit forms a separate compound with barium and oxygen. Therefore, $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_3$ was chosen as the next compound to be tested. This compound was prepared by reaction of the respective amounts of barium carbonate, cerium oxide, and neodymium oxide. Reaction was performed by heating the grounded mixture of powders at 1250°C for 5 hours in air. The initial weight of reagents was 112.6 grams. The weight of products was 97.5 grams which is close to the theoretical yield of 99.5 grams. The resulting compound is brown in color as is expected for compounds which incorporate neodymium. X-ray diffraction analysis indicated a single phase.

The next step was to attempt hot pressing the powder into a disk. Here again, problems were encountered in cooling the hot-pressed sample. Hot-pressed samples of doped barium-cerium are shown in Figure 10. In this case, no significant difference can be observed between results of hot pressing at 1350° and 1450°C. Because no satisfactory results were obtained by using hot pressing, the next step was cold pressing and furnace sintering. Particular attention was put on the particle size distribution of the powder and sintering was performed in air with the sample resting on a platinum foil. This process was successful and electrolyte disks were prepared with a density of at least 94% of the theoretical density of pure BaCeO_3 . The high density was confirmed by using water adsorption and Archimede's method. At this point in the program, two SSPC materials had been prepared and were available for evaluation, $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_3$.

4.2. Apparatus for Conductivity Measurements

The special apparatus was assembled for making conductivity measurements on SSPC's in order to ensure full control over the gas flow in the system.

Figure 10. HOT-PRESSED BARIUM-CERIUM BASED SAMPLES AFTER
HOT PRESSING AT 1350°C (Left) AND 1450°C (Right)

The apparatus consists of a cell holding device, the support, and the gas supply piping as shown in Figure 11. Alumina tubes were used and were specifically selected to fit inside one another as well as inside remachined Swagelok reducing bushings. Seals were obtained between the bushings and the alumina tubes by reversing the back ferrule and using an O-ring in place of the front ferrule. The bushings were drilled and a 1/4 inch tube was silver soldered in place in order to provide an exhaust port.

Thin slices were cut from a Pyrex tube for use as gaskets between the apparatus and the SSPC electrolyte. Pyrex glass is well suited for gas leak prevention because it softens in the temperature range of interest. Upon heating, the Pyrex softens and forms a seal between the 1/2 X 3/4 inch alumina tubes and the sample. Some concern was expressed about developing an electric shorting path through the Pyrex glass gasket. However, electrical conductivity data found in the literature indicates a conductivity less than $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in the temperature range of interest. Since this glass seal has a small contact area, its electrical conductivity can be neglected.

Special attention during the design of the apparatus was given to leak recognition. The reaction between oxygen from the oxidant gas and hydrogen from a fuel leak could produce water vapor and disturb the results significantly. This problem was solved by using an oxygen/argon mixture as the oxidant gas, and a hydrogen/nitrogen mixture as the fuel gas and monitoring both exhaust streams via gas chromatography. Finding argon in the fuel exhaust gas or nitrogen in the oxidant exhaust gas is indicative of a leak. Also, the annulus between the 3/8 X 1/2 inch alumina tube and the 1/2 X 3/4 inch tube were purged with helium. Detection of trace amounts of any other gas in the helium outlet stream is also indicative of a leak. Such precautions are necessary for the accurate measurement of the conductivity and the unequivocal assignment of ionic conductivity to mobil protons.

4.3. Strontium-Cerium Based Electrolyte

4.3.1. Electrode Fabrication

To answer questions about the conduction mechanism, solid palladium foils were chosen as preferred electrodes on both sides of ytterbium-doped strontium-cerium perovskite electrolyte. For all practical purposes, palladium is permeable only to hydrogen. Therefore, pumping hydrogen through

- A - THERMOCOUPLE
- B - $1/8" \times 1/4"$ ALUMINA TUBE
- C - SWAGelok REDUCING BUSHING WITH TUBE ADDED
- D - $1/2" \times 3/4"$ ALUMINA TUBE
- E - $3/4" \times 1"$ ALUMINA TUBE
- F - PYREX GASKET
- G - SAMPLE TO BE TESTED
- H - O-RING
- I - WIRE
- J - OXIDANT OUT
- K - OXIDANT IN
- L - FUEL IN
- M - FUEL OUT
- N - HELIUM OUT
- O - HELIUM IN

Figure 11. DESIGN OF APPARATUS FOR CONDUCTIVITY MEASUREMENTS

a short-circuited cell or with an externally applied voltage would be possible only if the majority of the conduction current results from proton conduction.

The first method tried for putting palladium on the faces of the disk involved suspending palladium black in n-butyl acetate. A few drops of this suspension was placed on the surface of the disk with an eye dropper and allowed to evaporate. This process was repeated until enough palladium black had been deposited to give a palladium coating 10 microns thick. (10 microns was chosen because it was feared that the current carrying lead wires could not be welded to anything thinner.) The sample was then heated to 800°C overnight. The palladium sintered, but also shrank. It covered about 25% of the disk's surface, was much thicker in the center than on the edges, and did not stick to the disk. Sputtering was tried next. It was discovered that under the conditions used, it would take about 80 hours of sputtering to put a 10 micron layer on one side of the sample. This amount of time was considered unacceptable.

The process was modified and a layer of palladium much less than 1 micron was sputtered on one side of the disk. A hole, whose diameter was less than the diameter of the disk, was cut in a piece of aluminum foil. This foil was placed over the disk before sputtering to prevent palladium from reaching the outer circumference of the disk and providing an electrical pathway (short) between the flat surfaces of the disk. This also prevent palladium from being sputtered to the outer edge of the flat surface. The sintering experiment with palladium in n-butyl acetate described above, was repeated using the sputtered surface in the hope that the sintered palladium would bond to the sputtered palladium. However, this did not happen.

A third attempt was made to produce a thick electrode by sputtering a palladium layer about 0.5 microns thick on one side of an electrolyte disk. The disk was placed between two pieces of palladium/silver foil which has a higher permeability to hydrogen than palladium. A weight was placed on top and the combination was heated in a 10% hydrogen/90% nitrogen mixture to 775°C in 11 hours and held there for 8 hours. However, the foil did not bond to the sputtered palladium.

Electroless plating was tried next using a disk on which a 0.5 micron layer of palladium had been sputtered. The outer circumference of the electrolyte disk was covered with rubber cement to prevent plating on the

outside. The disk was placed in an 80°C solution of palladium (II) acetate, ammonium hydroxide, EDTA di-sodium salt, hydrazine, and water. Both surfaces were plated, including an area on the flat surfaces which was not sputtered. When viewed by an optical microscope, the plating appeared continuous with no holes. However, the thickness, assuming equal plating on each side, was still less than 2 microns. The resistance across the diameter of each flat face was measured to be about 0.6 ohms and the room temperature resistance from face-to-face through the disk was measured to be greater than 20 meg ohms confirming that palladium had not deposited on the outer circumference. The disk weighed 0.975 g, was 0.466 inches (11.8 mm) in diameter, and 0.063 inches (1.60 mm) thick.

The idea of welding the lead wires to the surface was abandoned and a method was devised for attaching platinum current collector and voltage measuring wires by a spring contact. A spring was fabricated from a 0.042 inch (1.07 mm) diameter platinum wire. The spring was fashioned so that it is supported by the alumina tubes of the sample holder and could be pressed against the palladium surfaces. Platinum voltage and current measuring wires were welded to these springs.

Photographs of both sides of the sample are shown in Figure 12. A schematic diagram of measurement protocol is presented in Figure 13.

The strontium-cerium electrolyte disk with all-solid palladium electrodes was loaded into the test apparatus. The purpose of the experimental program undertaken was to test the experimental set up and to collect data helpful for the determination for the conduction mechanism. The platinum springs were compressed to insure good electric contact with palladium electrodes.

4.3.2. Concentration Cell Experiments

The system was heated to 700°C over 12 hours. Inert gases were passed through the anode and the cathode compartment. Helium was passed through the annulus compartment. After the operating temperature was reached the following gas flows were established:

Anode: Hydrogen (100%), flow rate 440 cc/min

Cathode: Argon (100%), flow rate 400 cc/min

A stable open circuit voltage (OCV) of 321 mV was observed at this condition.

Figure 12. PHOTOGRAPHS OF THE $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ ELECTROLYTE SAMPLE
WITH PALLADIUM ELECTRODES ON BOTH SIDES

Figure 13. SCHEME OF THE PROTON CONDUCTIVITY MEASUREMENTS
IN THE Pd/SSPC/Pd SYSTEM

Molecular sieves were placed in both anode and cathode gas inlets in order to remove trace amounts of water vapor. Two series of experiments with this hydrogen concentration cell configuration were performed. The cell was operated under various conditions for approximately 100 hours for the duration of the first (Exp 1) and second (Exp 2) experiments. Results are presented in Table 7.

Table 7. OCV OF THE HYDROGEN CONCENTRATION CELL AT 700°C WITH (Reduced Humidity Conditions) DRY ARGON AS AN INERT GAS

Hydrogen Mole Fraction		Open Cell Voltage, mv		
Anode	Cathode	Exp 1	Exp 2	Theory*
1.00	0.020	145		164
1.00	0.063		90	116
1.00	0.091	86		100
1.00	0.117		62.5	90
1.00	0.200		45	67
1.00	0.275	45		54
1.00	0.434	25		35
1.00	1.00	-2		0
1.00	1.00		-7	0

* Hydrogen concentration cell ($t_H = 1.0$ assumed).

The slope calculated for the relationship of $\ln (H_2/H_2')$ versus OCV using a regression curve is 37.7 mV for (Exp 1) and 34.3 mV for (Exp 2); respectively, compared with the theoretical slope of 41.9 mV ($RT/2F$). However, the lines do not intersect the x-axis at the origin. A small negative OCV is observed with pure hydrogen on both sides. The possible electrochemical reason for this situation is the existence of additional voltage generating cells in the system that produces this side effect. For example, the Pt/Pd junctions may be operating as a weak thermocouple.

At the completion of this part of the test, the cathode gas was switched back to pure dry argon. After 20 minutes, the OCV stabilized at about 325 mV. This is the equivalent of 350 ppm of hydrogen in the cathode gas, assuming that protons are the only ionic species being conducted. This is not an unreasonable result. Perovskite based SSPC electrolytes are known to have some electronic conductivity. Thus, despite the external electrical circuit

being open, some electrical current still flows internally and some hydrogen is transported from the anode side to the cathode side.

4.3.3. Fuel Cell Experiments

The next step in the experimental protocol called for oxygen to be introduced into the argon at the cathode side. Oxygen was introduced into the argon at a rate of approximately 75 cc/min ($P_{O_2} = 0.091$ atm) the OCV of the cell increased immediately to 1030 mV reaching 1100 mV after a period of 12 minutes.

After the voltage had stabilized, the fuel cell was externally loaded and the respective currents and voltages were measured. Results of the current/voltage measurements are presented in Figure 14. Based on the slope of this highly linear curve, the total resistance of the cell was calculated to be about 150 ohms. Assuming the active surface area of electrodes to be 0.5 cm^2 , the specific total conductivity can simply be calculated --

$$k = [(150) * (0.5)/(0.161)]^{-1} = 2.15 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ at } 700^\circ\text{C} \quad (23)$$

This calculated value is close to the value reported by Iwahara, 2.20×10^{-3} at this temperature. The 7.3 mA was the highest current obtained under short circuit conditions.

4.3.4. Inert Gas Experiments

The cell was returned to OCV conditions and dry inert gases were passed through both the anode and the cathode sides. This resulted in a floating voltage with measurements as high as -61.5 mV (note that the cell voltage has reversed). To clarify the origin of this voltage, the cell was short-circuited. Current flowed under this condition and decreased from an initial value of 0.14 to 0.03 mA in 30 seconds and after 20 minutes had dropped below the detection limit of the ammeter (0.01 mA). However, the initial voltage of -60 mV was recovered after returning to OCV conditions. Repetition of this experiment gave similar results. This behavior is typical for a process limited by concentration polarization and was attributed to the presence of water vapor in the annulus compartment. In the original design of this test stand, helium gas was to flow through the entire length of the annulus compartment purging all gases leaking from the cell. However, after

Figure 14. POLARIZATION CURVE OF THE STRONTIUM-CERIUM TYPE ELECTROLYTE
WITH ALL SOLID PALLADIUM ELECTRODES
(Conditions: Temperature = 700°C, dried gases)

the temperature reached 700°C, helium stopped flowing and overpressure built up in the purge system. Presumably, the softened glass gasket sealed not only the alumina/electrode interface but had flowed to block the annulus compartment as well. Therefore, water vapor laden air from the laboratory diffused back through the annulus exhaust tube, ("N" in Figure 11) into the annulus space and set up a local cell which became a "noise generator" driven by the concentration difference of water vapor at the anode (less than 10 ppm) and in the annulus. The decay in the current observed after short-circuiting the cell can be explained in terms of using up the limited amount of water vapor trapped in the annulus space.

The water vapor supply was assumed to be the rate determining step. Return to OCV conditions allowed slow diffusion of water vapor back into the annulus and the buildup of the cell voltage. Because of the small surface area of the annulus half of these local cells, they had negligible effects on measurements at conditions other than those with inert gases on both sides.

To test this hypothesis both the annulus inlet "O" and the annulus outlet "N" were connected to a flash of molecular sieves. The connections dead-ended in the flask. There was no gas exchange except via diffusion. Nevertheless, the OCV slowly returned to zero over a period of 100 minutes as shown in Figure 15.

A full understanding of this problem was gained and the problem solved by supplying dry helium to both the anode and cathode annulus spaces through concentric tubes passed through "N" and "O." Removal of water vapor from the annulus spaces eliminated the problem of a false OCV reading when inert gases were supplied to both anode and cathode compartments.

Experiments with the strontium cerium type electrolyte were continued with the reconfigured cell. A polarization curve for the cell with hydrogen/nitrogen mixture on the anode side and argon on the cathode side is presented in Figure 16. Slightly higher cell resistance was observed in this case.

4.3.5. Electronic Conductivity Measurements

The purpose of the next experiment was to estimate the electronic conductivity level in the electrolyte. For this purpose, inert, dried gases were supplied to the anode (nitrogen) and cathode (argon) at flow rates of

Figure 15. OCV RESPONSE AFTER PLACEMENT OF
MOLECULAR SIEVE IN THE ANNULUS GAS LOOP
(Solid square -- OCV after overnight cell operation)

Figure 16. POLARIZATION OF THE STRONTIUM-CERIUM TYPE FUEL CELL
WITH HYDROGEN/NITROGEN AT THE ANODE (0.117 atm/0.883 atm)
AND ARGON AT THE CATHODE (Dried Gases, Temperature, 700°C)

845 cc/min and 720 cc/min, respectively. An external voltage was applied to the electrodes and the resulting current was measured. Voltages from -600 mV to +600 mV were applied. The current was observed to change linearly with increasing voltage and passed through zero at zero applied voltage. A maximum current of 0.09 mA was measured at +600 mV. This is equivalent to an electronic transference number of --

$$t_e = 0.023 \pm 0.003 \quad (24)$$

or less. Dried helium was passed through the annulus compartments during these tests.

4.3.6. Oxygen Partial Pressure Experiments

During this experiment, pure hydrogen was supplied to the anode and oxygen mixed with argon was supplied to the cathode. Dry helium was purged through the annulus. The oxygen partial pressure supplied to the cathode compartment was varied from 0.03 to 0.15 atm while monitoring the OCV. No change in the OCV was noted with changing oxygen partial pressure. However, because the cathode was a solid palladium layer, there was no reason to believe that the OCV should have varied by more than a millivolt.

4.3.7. Experiments at 800°C

After completion of the above, the cell temperature was increased to 800°C. With dried hydrogen on the anode side (115 cc/min) and a low flow of argon on the cathode side of the cell (7.6 to 7.8 cc/min), an external voltage of about 1.00 V was applied. This should pump hydrogen through the cell from anode to cathode if protons are the conducting species but would be unable to sustain a current if oxide ions were the conducting species. The purpose of this experiment was to detect hydrogen on the cathode side of the cell by use of a gas chromatograph. At 945 mV of applied voltage, the current measured was 10 mA. A constant current was maintained during this experiment. Hydrogen was detected in the argon, but quantitative analysis of the result is uncertain because the hydrogen concentration was near the detection limit of the GC. The cell voltage required to maintain a constant current was observed to decrease continually from the beginning of the experiment reaching 830 mV after 30 minutes. This is the reverse of what would be expected for an oxide

ion conductor. When the cell was returned to open circuit, no hydrogen was detected in the cathode exhaust.

The next day, However, the cell did not respond. Therefore, after several attempts to recover OCV, the fuel cell was cooled down to room temperature over a 20 hour period and the test terminated.

4.3.8. Posttest Analysis

The cell was carefully disconnected to avoid electrode surface damages and pictures of both the anode and cathode side were taken. As can be seen from Figure 17, the cathode side of the cell which was operated at a potential equal to or more positive than the anode, seems to be intact with only a few small marks being visible. These marks probably resulted from the thermal stress during the heating up/cooling-down procedure or from the additional stress exerted by the spring used as a current collector. The rounded trace of the current collector contact with the cathode is apparent on the cathode surface. The glass gasket covers some electrode area close to the inner wall of the alumina tube presumably preventing hydrogen from gaining access to the surface. Figure 17 also shows the anode side of the cell. The anode surface is damaged and the underlying electrolytes face is clearly visible in a few places. The nature of the damages to the palladium layer is typical of gas evolution processes occurring at the at the Pd/electrolyte interface.

Summary of the Fuel Cell Dimensional Specifications

- Electrolyte thickness = 0.063 inch (0.160 cm)
- Inside (average) diameters of an alumina tube:
 - Anode: 0.37 inch (0.94 cm)
 - Cathode: 0.37 inch (0.94 cm)
- Active surface area of electrodes (not covered by softened glass gasket) was calculated based on electrode pictures
 - Anode surface = 0.49 cm^2
 - Cathode surface = 0.52 cm^2
- Palladium layer thickness -- less than 2 microns

4.3.8. Discussion of Results for Strontium-Cerium Oxide

In retrospect, the final experiment was probably a bad idea. It is possible that the applied voltage electrolyzed the strontium-cerium oxide,

Figure 17. POSTTEST VIEWS OF THE ANODE (Top) AND THE CATHODE (Bottom)
SIDE OF THE CELL WITH THE STRONTIUM-CERIUM
ELECTROLYTE AND SOLID FOIL ELECTRODES

reducing the cerium and evolving oxygen at the anode. Oxygen, unable to diffuse through the palladium, formed a gas pocket at the electrode/electrolyte interface and lifted the Pd foil off the surface. The same effect could be achieved, however, if the electrolyte were an oxide ion conductor. Since it was possible to pump hydrogen from the anode to the cathode, the possibility of strontium cerium oxide being only an oxide ion conductor can be eliminated. On the other hand, the possibility that it is a mixed proton/oxide ion conductor cannot be ruled out. It is also possible that hydroxide ions act as "vehicle" ions for the transfer of hydrogen from anode to cathode, however, such a vehicular transport mechanism would require a counterflow of oxide ions from cathode to anode since there is no evidence for either oxygen or water vapor evolution at the cathode/electrolyte interface.

The ionic transport number for this electrolyte was about 0.97 and the electronic transport number about 0.03 at 700°C. This is well within the range of acceptability for a practical fuel cell device. Unfortunately, the total ionic conductivity is still about an order-of-magnitude too low. To fabricate a practical fuel cell device from doped strontium-cerium oxide would require that the electrolyte be less than 10 microns thick.

4.4. The Barium-Cerium Based Electrolyte With Solid Foil Electrodes

A proton conductor fuel cell based on 15% neodymium-doped barium cerium oxide (BCN) was operated for approximately 200 hours. Solid foil palladium electrodes were deposited on both sides of the electrolyte. The electrolyte thickness was approximately 30 mils (0.75 cm). Visual examination of the electrode before cell assembly showed shiny and smooth palladium surfaces. The system configuration was generally the same as previously described with some minor changes in the piping system to allow humidification of gases at 0°C. Also, a groove was cut on the inside of the outer alumina tube to provide a gas passage past the electrolyte disk should the Pyrex gaskets again extrude into the annulus space. This proved to be effective and the problem did not recur. The cell was slowly heated up to 700°C in inert gases. No significant leaks were detected during the course of the experiment. Both hydrogen concentration cell as well as hydrogen/oxygen fuel cell experiments were performed at 700°, 750°, 800°, and 850°C. No changes in the fuel cell performance were observed other than those expected from the gas composition changes or changes in the temperature. Experimentation was terminated

prematurely when the oven failed during the night and the cell cooled to room temperature in about 1 hour. The cell was then disassembled and photomicrographs of the electrode surfaces were taken.

4.4.1. The Hydrogen Concentration Cell

The cell was first operated as a hydrogen concentration cell on open circuit in the temperature range of 700° to 850°C. The most significant trend observed during the test was the increasing difference between experimental measurements and theoretical predictions at higher temperatures (See top and bottom plots in Figure 18). The theoretical curves were calculated assuming 100% protonic conduction in the electrolyte, that is --

$$OCV = \frac{RT}{2F} \ln \frac{pH_2, \text{ an}}{pH_2, \text{ cath}} \quad (25)$$

The quantitative data are shown in Table 8.

The data presented in Table 8 can be compared to data presented by Iwahara.¹⁶³ For a similar electrolyte composition, Iwahara claims 20% oxide ion conduction at 800°C. The remaining fraction of the conductivity is proposed to be proton conduction. Experiments performed at IGT confirm that only about 80% of the theoretical voltage of the hydrogen concentration cell can be obtained. However, based on IGT's current results, the mechanism responsible for the remaining 20% of the conduction cannot be determined.

The next experiment was to load the hydrogen concentration cell and use it as a pump. The cell was operated at 800°C with 28 mole percent hydrogen in argon (humidified at 0°C) passed through the anode and with nitrogen (humidified at 0°C) passed through the cathode gas compartment. A flow of 34 cc/min of nitrogen was maintained during the experiment.

At OCV, the nitrogen was found to contain 0.08% hydrogen (GC measurements). This result was interpreted as indicating hydrogen diffusion through the 94% dense electrolyte equal to approximately 0.029 cc H₂/min. The cell was short circuited and a steady-state current of 5.1 mA was observed at approximately 20 mV of cell voltage. The short circuit voltage was not zero because of resistance in the lead wires. At short circuit, after steady-state conditions were established, the nitrogen was found to contain 0.21% hydrogen. This is an equivalent of 0.071 cc H₂/min. Therefore, the net

Figure 18. RESULTS OF OPERATION OF THE HYDROGEN CONCENTRATION CELL AT 700°C (TOP) AND 800°C (BOTTOM) COMPARED TO THEORETICAL CURVE ASSUMING 100% PROTON CONDUCTION. HYDROGEN CONCENTRATION RATIO WAS CALCULATED FROM THE FLOW METER READINGS (Δ) OR GC MEASUREMENTS (▲) THE BCN ELECTROLYTE WITH SOLID FOIL ELECTRODES.

Table 8. THEORETICAL AND EXPERIMENTAL DATA FOR THE OCV OF THE PCFC (BCN, Nd = 15%) WITH SOLID FOIL ELECTRODES

Temp, °C	OCV Slope, Theory, s_t	mV/decade Exper., s_e	Correlation Factor	Ratio s_e/s_t
700	41.9	38.3	0.998	0.93
800	46.4	36.3	0.996	0.79

hydrogen flow through the cell is equal to 0.042 cc H₂/min. This increase in hydrogen flow can be attributed only to protonic conduction when solid Pd electrodes are used. This number is close to the theoretical value of 0.036 cc H₂/min based on 5.1 mA, taking into account the nitrogen flow fluctuations and the uncertainty in the GC measurements at lower concentrations, this can be taken as evidence that proton conduction accounts for a majority of the BCN electrolyte conduction.

Polarization curves for the hydrogen concentration cell at various temperatures are presented in Figure 19. The linear behavior of the cell through the full voltage range can be attributed to low activation polarization of the electrodes.

4.4.2. Hydrogen/Air Fuel Cell

Data obtained from operating the cell in a fuel cell configuration, H₂, Ar/Pd/BCN/Pd/Air, in the temperature range 700° to 850°C are presented in Figure 20. A detailed comparison of the results is presented in Table 9. The experimental OCV to theoretical OCV ratio decreases with increasing temperature. Polarization curves are very linear at all temperatures leading to high correlation factors for linear regression calculations. To calculate activation energy for conduction, results of resistance calculations, R, have been presented in the logarithmic scale as a function of inverse temperature. The data and the linear regression line are presented in Figure 21. The following equation was calculated to fit the data:

$$\ln(R) = -3.75 + 7498/T, \text{ ohms} \quad (26)$$

or

$$R = 0.0236 \exp(7498/T), \text{ ohms} \quad (27)$$

Figure 19. POLARIZATION CURVES FOR HYDROGEN CONCENTRATION CELL WITH SOLID FOIL ELECTRODES TAKEN AT VARIOUS TEMPERATURES. HYDROGEN CONCENTRATIONS: ANODE-50%, CATHODE-3%. HYDROGEN MIXED WITH INERT GAS AND HUMIDIFIED AT 0°C.

Figure 20. POLARIZATION CURVES FOR THE BCN BASED FUEL CELL OPERATED WITH SOLID FOIL ELECTRODES WITH 30% H_2 /70% Ar FUEL MIXTURE AND AIR; BOTH GASES HUMIDIFIED AT 0°C. CONTINUOUS LINES ARE OBTAINED BY THE LEAST SQUARE REGRESSION

Table 9. COMPARISON OF EXPERIMENTAL RESULTS OF THE FUEL CELL
30% H₂, 70% Ar (Humidified at 0°C)/Pd/BCN/Pd/AIR
(Humidified at 0°C) OPERATED AT VARIOUS TEMPERATURES

Temp, °C	Open Cell Voltage, mV		Regression Analysis Results			OCV Ratio E_e/E_t
	Measured, E_e	Theory, E_t ¹	OCV ² , mV	R , ohm ³	R-square ⁴	
700	1000	1130	980	51.1	0.9976	0.89
750	960	1122	965	37.1	0.9999	0.86
800	924	1115	940	25.6	0.9984	0.83
850	904	1107	915	18.4	0.9992	0.82

¹ Calculated assuming 100% proton conduction of the electrolyte.

² OCV from the intersection of the least squares line with the zero current line.

³ Total resistance of the fuel cell from the slope of E versus i plot.

⁴ Correlation factor.

with the correlation of 0.997. Specific conductivity is:

$$\sigma = d/(RS), \text{ ohm}^{-1} \text{ cm}^1 \quad (28)$$

where:

d = Electrolyte thickness, 0.75 cm

S = Active surface area, approximately 0.57 cm²

Substituting respective values into Equation 28 leads to the equation for specific conduction of the BCN (Nd = 0.15%) electrolyte.

$$\sigma = 5.58 \exp (-61.9 \text{ kJ/mol}/R_c T), \text{ ohm}^{-1} \text{ cm}^{-1} \quad (29)$$

where R_c = gas constant.

The actual pre-exponent is probably higher than that calculated here. This is because the active surface area of the electrodes was taken to be the entire geometrical area. Also, electrode polarization is assumed to be zero. Therefore, the specific conductivity of BCN (Nd = 0.15%) is greater than 0.0025 ohm⁻¹ cm⁻¹ at 700°C, than 0.0051 ohm⁻¹ cm⁻¹ at 800°C, and greater

Figure 21. ACTIVATION ENERGY PLOT. THE RESISTANCE (Logarithmic Scale) OF THE BCN-BASED FUEL CELL AS A FUNCTION OF INVERSE TEMPERATURE. CONTINUOUS LINE IS A LEAST SQUARE REGRESSION LINE. EXPERIMENTAL CONDITIONS THE SAME AS LISTED IN FIGURE 20

than $0.0093 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 900°C . The activation energy for the conduction process in the temperature range 700° to 850°C has been calculated to be 61.9 kJ/mol or 0.64 eV . This is slightly higher than the activation energy of 0.54 eV which is calculated for BCN doped with only 10% Nd from Iwahara's data.¹⁶³

4.4.3. The Fuel Cell Performance Analysis

The BCN fuel cell was operated at 500 mV, and delivered an average current density of 40 mA/cm^2 at 850°C and an average current density of 22 mA/cm^2 at 750°C .

Several factors influenced the cell performance. The most severe limitation on the cell performance was high electrolyte resistance, due to the relatively large electrolyte thickness, 30 mils (0.075 cm). Posttest analysis of the electrodes showed multiple areas of surface deterioration. Pictures of the anode and the cathode sides of the posttest cell are presented in Figures 22 and 23. Three main surface deterioration can be distinguished:

- a. Multiple "bubble" type deformations of the foil electrode occurred on the anode of the cell. Microscopic examination of these "bubbles" leads to the conclusion that gas was generated under the non-porous palladium surface. This process can significantly limit contact at the electrode/electrolyte interface and leads to severe performance limitations.
- b. A narrow crack is visible on both sides of the electrolyte. This crack probably resulted during rapid cell cooling after the oven failure since no significant gas cross-over was observed during the experiment.
- c. Severe electrode surface damage, including loss of contact with the electrolyte surface was observed on both anode and cathode where the current collecting spring touched the electrode surfaces. This delamination probably occurred during cell disassembly.

The damaged surfaces have been included in the current density calculations. Therefore, real current densities are probably higher than those reported.

Data presented in Figures 19 and 20 show highly linear cell polarization curves for both the hydrogen/air fuel cell and the hydrogen concentration cell. This may have resulted from the use of palladium electrodes on both sides which result in very low electrode polarizations. However, Iwahara¹⁶³ has reported low polarization with nickel electrodes as well and considers low interfacial losses between electrode and electrolyte as being one of the major

**Figure 22. POSTTEST VIEW OF THE ANODE SIDE OF THE PCFC
WITH THE BCN ELECTROLYTE AND SOLID FOIL ELECTRODES**

Figure 23. POSTTEST VIEW OF THE CATHODE SIDE OF THE PCrC
WITH THE BCN ELECTROLYTE AND SOLID FOIL ELECTRODES

attributes of SSPC fuel cells. Linear characteristics are observed throughout the full range of cell operation (OCV to short circuit).

4.5. The Barium-Cerium Based Electrolyte With Porous Electrodes

In the last section (4.4) the results of measurements on a PCFC using a 15% neodymium doped barium cerium oxide (BCN) electrolyte with non-porous palladium electrodes was presented. Examination of the electrodes after the experiments revealed that both electrodes were changed. The damage could have been caused by generation of gas under the non-porous palladium; that is, at the electrolyte-electrode interface. Nevertheless, relatively good cell performance was measured. Oxygen and/or water vapor could be formed at the interface and cause the damage if even small amounts of hydroxide ion and/or oxide ion conduction occurred.

In this test, voltage and current measurements were made using a BCN electrolyte of the same composition but with porous palladium electrodes. Now, if gas is produced at the electrolyte-electrode interface, it should escape without damaging the electrode. It was expected that the performance of this cell would be better than the last one. This cell gave a reasonable performance early in the 440 hour test but the performance degraded.

However, in this cell, a platinum wire gauze was placed between the porous electrodes and the platinum spring current collector. Figure 24 is a posttest photo of the top and bottom views of the cell. In the top view, the BCN cell is obscured by the wire gauze. The designation "Top" and "Bottom" are used in place of "Anode" and "Cathode" because of the wider range of gas compositions used and because, in some cases, the compositions were purposely reversed in consecutive experiments.

The electrode material on top was loose and not well sintered nor tightly bonded to the electrolyte. Much of the electrode material was missing from the bottom of the electrolyte. It is not clear if this occurred during operation or during disassembly. However, its occurrence during operation would account for the degradation in cell performance.

Although the performance degraded, the output was stable over the time of individual experiments. Thus, meaningful data was collected to evaluate the cell as a hydrogen concentration cell and to study the conduction mechanism; that is, to determine the fraction of the conductivity due to ions other than

Figure 24. POSTTEST VIEW OF THE BCN TYPE FUEL CELL
WITH POROUS ELECTRODES

protons. Representative OCV data are presented in Tables 10 and 11 at 700° and 800°C and in Figure 25.

At 800°C, the annulus gas was changed from 0.094% H_2 in He to dry He and then back to the initial annulus gas composition in order to determine the effect of the annulus gas on the OCV measurements. Within experimental error, no effect of annulus gas on the fuel cell OCV was found. The system was continually checked for leaks by means of GC analysis of the outlet gases from the electrode gas compartments and the annulus. No evidence for leaks was found.

The comparison of measured OCV slope of the hydrogen concentration cell with the theoretical slope is presented in Table 12.

The data presented in Table 12 can be compared with the similar set of data presented in Table 8 for the system with solid electrodes. Better data correlation and higher proton transference numbers, s_t/s_e , are apparent. This discrepancy may be caused by gas buildup below the surface of the foil electrodes, diluting hydrogen and decreasing the OCV. The effect is especially striking at 800°C where the values of proton transference number are 0.79 and 0.95 for the solid and porous electrodes, respectively. An alternative explanation is that the small hydrogen leak present in the BCN electrolyte in the solid electrode experiment caused the OCV measurements to be low. No such leak was present in the porous electrode experiments described above.

Table 10. REPRESENTATIVE OCV MEASUREMENTS OF A 15% NEODYMIUM-DOPED BARIUM CERIUM OXIDE PCFC WITH POROUS PALLADIUM ELECTRODES AT 700°C

Cell Top		Cell Bottom		OCV, mV
Composition, mol %*	Humidification Temperature, °C	Composition, mol %*	Humidification Temperature, °C	
Air, 100	Dry**	H ₂ , 10.19	32	-976
N ₂ , 100	0	N ₂ , 100	0	-0.3
N ₂ , 100	0	N ₂ , 100	35	-1.3
N ₂ , 100	Dry	N ₂ , 100	35	-1.5
H ₂ , 0.0889	Dry	H ₂ , 0.0889	35	38.3
H ₂ , 0.0889	0	H ₂ , 0.0889	35	10.8
Air, 100	0	Air, 100	35	-33.1
Air, 100	Dry	Air, 100	35	-45.6
Air, 100	0	O ₂ , 100	35	-18.4
O ₂ , 100	0	Air, 100	35	-37.8
H ₂ , 10.19	0	H ₂ , 10.19	35	12.7
H ₂ , 10.19	Dry	H ₂ , 10.19	35	40.6
H ₂ , 10.19	0	H ₂ , 10.19	0	-3.6
H ₂ , 1.03	0	H ₂ , 1.03	0	-3.2
H ₂ , 3.10	0	H ₂ , 1.03	0	41.5
H ₂ , 10.19	0	H ₂ , 1.03	0	91.4
H ₂ , 30.17	0	H ₂ , 1.03	0	136
H ₂ , 100	0	H ₂ , 1.03	0	185
H ₂ , 10.19	0	H ₂ , 10.19	53	17
Air, 100	0	Air, 100	53	-56
O ₂ , 100	0	Air, 100	53	-63
Air, 100	0	O ₂ , 100	53	-36
Air, 100	0	H ₂ , 10.19	53	-962
Air, 100	0	H ₂ , 10.19	53	-961

* Mol % before humidification.

** Dry is not thermodynamically well-defined, but the gas was dried by passing through molecular sieves.

Table 11. REPRESENTATIVE OCV MEASUREMENTS OF A 15% NEODYMIUM-DOPED BARIUM CERIUM OXIDE PCFC WITH POROUS PALLADIUM ELECTRODES AT 800°C

Cell Top		Cell Bottom		OCV, mv
Composition, mol %*	Humidification Temperature, °C	Composition, mol %*	Humidification Temperature, °C	
Air, 100	0	H ₂ , 10.19	53	-878
Air, 100	0	Air, 100	53	-34
Air, 100	Dry**	Air, 100	53	-39
Air, 100	Dry	O ₂ , 100	53	-25
Air, 100	0	O ₂ , 100	53	-20
O ₂ , 100	0	Air, 100	53	-41
H ₂ , 10.19	0	H ₂ , 10.19	53	48
H ₂ , 10.19	0	H ₂ , 10.19	0	-5.6
H ₂ , 1.03	0	H ₂ , 1.03	0	-5.7
H ₂ , 3.10	0	H ₂ , 1.03	0	42.4
H ₂ , 10.19	0	H ₂ , 1.03	0	96.5
H ₂ , 30.17	0	H ₂ , 1.03	0	143
H ₂ , 100	0	H ₂ , 1.03	0	192
H ₂ , 10.19	0	H ₂ , 10.19	35	33
Air, 100	0	Air, 100	35	-20
O ₂ , 100	0	Air, 100	35	-26
Air, 100	0	O ₂ , 100	35	-9
Air, 100	0	O ₂ , 100	35	-10
Changed annulus gas from dry 0.094% H ₂ in He to dry He				
Air, 100	0	O ₂ , 100	35	-10
O ₂ , 100	0	Air, 100	35	-27
O ₂ , 100	0	Air, 100	35	-26
Air, 100	0	Air, 100	35	-19
Air, 100	0	Air, 100	0	-1.4
Changed annulus gas from dry He to dry 0.094% H ₂ in He				
Air, 100	0	H ₂ , 10.19	0	-925

* Mol % before humidification.

** Dry is not thermodynamically well-defined, but the gas was dried by passing through molecular sieves.

Figure 25. OCV OF THE BCN TYPE FUEL CELL WITH POROUS ELECTRODES OPERATING AS A HYDROGEN CONCENTRATION CELL
 Continuous lines - theoretical values
 Experimental Results: Δ - at 800°C, $\square$ - at 700°C; Humidification temperature 0°C, TOP-top electrode, BOT-bottom electrode compartment

Table 12. THEORETICAL AND EXPERIMENTAL DATA FOR THE OCV OF
THE SSPC (BCN, ND = 15%) WITH POROUS ELECTRODES

Temp, °C	OCV Slope, mV/decade		Factor	Correlation Ratio
	Theory, s_t	Experiment, S_e		s_t/s_e^*
700	41.9	41.9	0.9998	1.000
800	46.2	44.1	0.999	0.954

* This ratio approximate proton transference number t_p .

5.0. CONDUCTION MECHANISM

It is clear from both the literature review and from the foregoing experimental work that the perovskites, and BaCeO_3 in particular, represent promising new solid-state electrolytes for fuel cell applications. It is not clear from the literature, however, that BaCeO_3 is a proton conductor. Iwahara¹⁶³ holds that below 800°C , this material is a proton conductor but above this temperature conduction is mixed proton and oxide ion. Bonanos et al.⁸⁰ hold that SrCeO_3 and BaCeO_3 are primarily oxide ion conductors with some hydrogen transported by a vehicular mechanism in which the proton is attached to an oxide vehicle to form a hydroxide ion. Sammels et al.¹⁶⁴ have proposed a dual mechanism in which hydroxide ions are transported from anode to cathode and oxide ions are transported simultaneously from cathode to anode.

What all of these authors seek to explain is the production of small amounts of water vapor at the anode of BCN based fuel cells. If BaCeO_3 were purely a proton conductor, all water vapor would be formed at the cathode. If it were only a oxide ion conductor, all water vapor would form at the anode. In fact, water vapor is produced at both electrodes of a BCN electrolyte fuel cell arguing for mixed conduction at temperatures above 800°C . The blistering of the solid foil anodes in both the SrCeO_3 (Figure 17) and the BaCeO_3 experiments (Figure 22) discussed above is clear evidence that gases other than hydrogen were evolved at the anode. However, since oxygen does not transport through solid palladium, it is unclear how water vapor could form at the anode/electrolyte interface by an oxide ion conduction mechanism, if there is no source of oxide ions at the cathode/electrolyte interface.

On the other hand, the behavior of the SSPC cells tested here is fully consistent with proton conduction. The proton transport number of 1.00 at 700°C and 0.954 at 800°C obtained in the final experiment using porous palladium electrodes, strongly supports a proton conduction mechanism. The most important support for a proton conduction mechanism, however, comes not from the experiments with hydrogen present, but from the experiments in which no hydrogen was used and an oxidizing atmosphere was present at both electrodes.

Twelve of the experiments listed in Tables 10 and 11 were conducted with oxidizing environments at both electrodes, six at 700°C and six at 800°C . In

these experiments the oxygen partial pressure was varied from 0.179 atm to 0.994 atm and the water vapor pressure was varied from 0.006 atm to 0.141 atm. Three cases can be defined and used for the interpretation of the experimental results. These cases are based upon the assumption of proton, hydroxide, or oxide ion conductivity and the attendant half reactions occurring at each electrode. The cases are as follows:

Case I. Proton Conduction

Case II. Hydroxide Ion Conduction

Case III. Oxide Ion Conduction

It is important to note that in Case II it is assumed that the hydroxide ions are formed and consumed in the electrodes and enter and exit the electrolyte as a unit. If the hydroxide ions are formed by proton transfer from the electrode to the electrolyte and only exist in the electrolyte, then the half reactions which are operative are those defined in Case I.

Nernst equations were derived for each of the three sets of half reactions and used to predict the OCV (EMF) for each of the 12 experiments. The results are summarized in Table 13 with the column marked "Exp." containing the actual experimentally determined EMF. The data from Table 13 are also depicted in a graphical format in Figures 26 and 27, but with the sign of the voltage reversed for purposes of clarity.

Although the experimental measurements do not match any of the predictions, it is apparent from Figure 26 that, as gas compositions are changed at 700°C, the EMF moves in lock-step with the Case I predictions. In other words, at 700°C, the BCN electrolyte is behaving like a proton conductor. At 800°C, the data qualitatively supports Iwahara's position that some oxide

Table 13. COMPARISON OF EXPERIMENTAL AND THEORETICAL EMF FOR THE BCN ELECTROLYTE BASED FUEL CELL WITH POROUS ELECTRODES

Gas Composition (mol %)											
Top Electrode		Bottom Electrode		Temperatures							
O ₂	H ₂ O	O ₂	H ₂ O	Exp.	I	780°C		Exp.	800°C		III
						II	III		I	II	
20.8	0.6	17.9	14.1	-56	-135	-129	+3	-34	-149	-142	+3
99.4	0.6	17.9	14.1	-63	-168	-96	+36	-20	-185	-106	+40
20.8	0.6	85.9	14.1	-36	-103	-162	-29	-25	-113	-179	-32
20.8	0.6	94.5	5.54	-18	-61	-125	-32	-9	-67	-138	-35
20.8	0.6	19.8	5.54	-33	-94	-92	+1	-20	-104	-101	+1
99.4	0.6	19.8	5.54	-38	-59	-127	+34	-26	-140	-65	+37

conductivity is also present and a mixed potential is observed. But even here, proton conductivity appears to exert the strongest influence.

In Iwahara's proposed mechanism, as in Case I above, the mobile ion (proton) is generated simultaneously with the production of oxygen. Therefore, in a strongly oxidizing environment, the number of mobile ions will be small and any incipient electronic conductivity present in the sample will serve to lower the measured EMF. However, it will not alter the direction of the response the cell makes to changes in gas composition.

A similar argument cannot be made for the proposition that BCN is an oxide ion conductor. The conditions used in these 12 experiments are excellent for supporting oxide ion mobility and exact correspondence between measured values and the Case III calculated values would be expected in the above experiments for an oxide ion conductor.

Sammells, et al. have not published a detailed description of their dual ion mechanism. Consequently, its merit cannot be determined. However, the results discussed above clearly indicate that if hydroxide acts as a vehicular ion to move hydrogen from the anode to the cathode, the hydroxide ion must be generated by the reaction of a proton with an oxide ion within the electrolyte lattice, and furthermore, that the only ionic species crossing the electrode/electrolyte interface is a proton.

Figure 26. EXPERIMENTAL VERSUS THEORETICAL EMF FOR BCN DEVICE AT 700°C

Figure 27. EXPERIMENTAL VERSUS THEORETICAL EMF FOR BCN DEVICE AT 800°C

The mechanism by which the proton moves through the electrolyte is of academic interest. Whether it tunnels from one discrete location to another, or hops from oxide ion to oxide ion existing in the interim as a hydroxide, or whether it moves as a hydroxide ion in a concerted dual-ion mechanism is important to IGT's understanding of this class of electrolytes. Unfortunately, the exact mechanism by which the proton moves through the electrolyte could not be determined from this work. What has been shown is that only protons cross the electrode/electrolyte interface in those mechanistic steps responsible for transporting hydrogen from the anode to the cathode. From a practical point of view, if protons disappear at the anode and reappear at the cathode of a BCN based fuel cell, the electrolyte qualifies as a proton conducting electrolyte.

6.0. CONCLUSIONS

During the course of this 2 year program a significant amount of SSPC work was performed worldwide. At present, neodymium doped barium cerium oxide is the best proton conductor on record. Iwahara's¹⁶³ reported conductivity of $3.5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 900°C for $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_3$ is somewhat better than the $9.3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ observed in this present work for $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_3$ and approaches the values required for a practical device. The work with solid metallic anodes performed here has demonstrated that the requirement for a three-phase interface of electrode, electrolyte, and fuel gas which is so restrictive in the oxide ion conducting YSZ fuel cell, is not a requirement for SSPC fuel cells. In SSPC fuel cells the proton can be generated within the anode material itself and injected into the electrolyte with only small polarization losses. The elimination of the need for an optimized three-phase interface has the potential of greatly simplifying the anode fabrication process to one of simple metallization.

Additional work is required, however. Practical and inexpensive methods of fabricating thin films of BCN must be found and a more serviceable cathode must be developed which can operate at 700°C and does not require noble metals. Although efforts to fabricate a BaThO_3 electrolyte failed, this material still holds the promise of higher ionic conductivities than BCN and warrants further investigation.

7.0. REFERENCES CITED

1. Jensen, J., "Actual and Potential Uses of Solid State Protonic Conductors" (in:) Solid State Protonic Conductors III for Fuel Cells and Sensors. Odense University Press, Denmark, 1985.
2. Iwahara, H., Uchida, H. and Tanaka, S., Solid-State Ionics 9/10 (1983) 1021.
3. Uchida, H., Tanaka, S. and Iwahara, H., J. Appl. Electrochem. 15 (1985) 93.
4. Iwahara, H., Uchida, H. and Tanaka, S., J. Appl. Electrochem. 16 (1986) 663.
5. Ohta, T. and Abe, I., Int. J. Hydrogen Energy 10 (1985) 275.
6. Gonzales, E. R. and Srinivasan, S., Int. J. Hydrogen Energy 9 (1984) 215.
7. Nakamura, O. and Ogino, I., Solid State Ionics 6 (1982) 337.
8. Nuttal, L. J. and McElroy, J. F., Int. J. Hydrogen Energy 8 (1983) 609.
9. Iwahara, H., Uchida, H. and Maeda, N., J. Power Sources 7 (1982) 293.
10. Takahashi, T., Tanase, S., Yamamoto, O., Yamauchi, S. and Kabeya, H., Int. J. Hydrogen Energy 4 (1979) 127.
11. Iwahara, H., Uchida, H. and Maeda, N., Solid State Ionics 11 (1983) 109.
12. Montoneri, E., Salzano, F. J., Findl, E. and Kulesa, F., Solid State Ionics 18/19 (1986) 994.
13. Findl, E., Kulesa, F. and Montoneri, E., Proceedings of the 19th Annual Intersociety Energy Conversion Engineering Conference, San Francisco, August 19-24, 1984.
14. Iwahara, H., Uchida, H. and Yamasaki, I., Int. J. Hydrogen Energy 12 (1987) 73.
15. Iwahara, H., Esaka, T., Uchida, H. and Maeda, N., Solid State Ionics 3/4 (1981) 359.
16. Ohta, T. and Sastri, M.V.C., Int. J. Hydrogen Energy 4 (1979) 489.
17. Uchida, H., Maeda, N. and Iwahara, H., J. Appl. Electrochem. 12 (1982) 645.
18. Iwahara, H., Uchida, H. and Kondo, J., J. Appl. Electrochem. 13 (1983) 365.
19. Oi, R., Electrochemical Materials, Ann. Rev. Mater. Sci. 16 (1986) 185.

20. Iwahara, H., Esaka, T., Uchida, H., Yamauchi, T. and Ogaki, K., Solid State Ionics 18/19 (1986) 1003.
21. Wallace, W. E., "Hydrogen Absorption by Intermetallic Compounds" (in:) "Solid State chemistry: A Contemporary Overview," Advances in Chemistry Series 186, A.Ch.S., Washington, 1980, p. 207.
22. Sen, B. K. and Sen, S., Solid State Ionics 18/19 (1986) 1025.
23. Sen, B. K. and Sen, S., Solid State Ionics 18/19 (1986) 1025.
24. McGeehin, P. and Hooper, A., J. Mat. Sci. 12 (1977) 1.
25. Shilton, M. G. and Howe, A. T., Mat. Res. Bull. 12 (1977) 701.
26. Krauer, K. D., Weppner, W. and Rabenau, A., Solid State Ionics 3/4 (1981) 353.
27. Krauer, K. D., Weppner, W. and Rabenau, A., Mat. Res. Bull. 17 (1982) 501.
28. Yde-Anderson, S., Skou, E., Krogh Anderson, I. G. and Krogh Anderson, E., "Protom Conduction in Ammonium Zedites" (in:) Solid State Protonic Conductors III -- for Fuel Cells and Sensors, Odense University Press, Denmark, 1985.
29. Takahashi, T., Tanase, S., Yamamoto, O. and Yamauchi, S., J. Solid State Chem. 17 (1976) 353.
30. Daniel, M. F., Desbat, B. and Lassegues, J. C., "Triethylenediamine Salts" (in:) Solid State Protonic Conductors III -- for Fuel Cells and Sensors. Odense University Press, Denmark, 1985.
31. Sai, Y. T., Smoot, S., Whitmore, D. H., Tarczon, J.D.C. and Halperin, W. P., Solid State Ionics 9/10 91983) 1033.
32. Farrington, G. C. and Briant, J. L., (in:) Fast Ion Transport in Solids, Vashisthta, P., Mundy, J. H. and Shenoy, G. K., ed., North-Holland, Amsterdam, (1979).
33. Baffier, N., Badot, J. C. and Colomba, Ph., Solid State Ionics 13 (1984) 233.
34. Lenfant, P., Plas, D., Ruffo, M., Colombar, Ph. and Boilot, J. P., Mat. Res. Bull. 15 (1980) 1817.
35. Thomas, J. D., Frase, K. G., McIntyre, G. J. and Farrington, G. C., Solid State Ionics 9/10 (1982) 1029.
36. Furukawa, Y., Nakabayashi, Y., Kawai, S. and Nakamura, O., Solid State Ionics 7 (1982) 219.
37. Baffier, N., Badot, J. C. and Colomba, Ph. Solid State Ionics 2 (1980) 107.

38. Colombari, Ph., Boillot, J. P., Chagnon, P. and Guillotenau, G., Bull. Soc. France Ceram. 119 (1978) 3.
39. Bates, H. P., Dudney, N. J. and Wang, J. C., J. Appl. Phys. 58 (1985) 4587.
40. Alberti, G., Casciola, M., Constantino, V. and Leonardi, M., "A. C. Conductivity of Anhydrous Pellicular Zirconium Phosphate in Hydrogen Form" (in:) Solid State Protonic Conductors III -- for Fuel Cells and Sensors, Odense University Press, Denmark, 1985.
41. Baranov, A. L., Shuvalov, L. A., Shchagina, N. M., Zh. Eks. Teor. Fiz. Pisma 36 (1982) 381.
42. Hainovsky, N. G., Yu, T., Pavlukhin, T. and Hairtdinov, E. F., Solid State Ionics 20 (1986) 249.
43. Bradley, R. S., Munro, D. C. and Ali, S. I., J. Inorg. Nucl. Chem. 32, (1970) 2513.
44. Lal, M. and Howe, A. T., J. Solid State Chem. 51 (1984) 155.
45. Weller, M. T. and Dickens, P. G., Solid State Ionics 9/10 (1983) 1081.
46. Slade, R.C.T., Halstead, T. K. and Dickens, P. G., J. Solid State Chem. 34 (1980) 183.
47. Mari, C. M., Bonino, F., Catti, M., Pasinetti, R. and Pizzini, S., Solid State Ionics 18/19 (1986) 1013.
48. Nakamura, O., Kodama, T., Ogino, I. and Mylake, Y., Chemistry Letters (1979) 17.
49. Nakamura, O., Ogino, I. and Kodama, T., Solid State Ionics 3/4 (1981) 347.
50. Weller, M. T. and Dickens, P. G., Solid State Chem. 60 (1985) 139.
51. Lal, M. and Howe, A. T., J. Solid State Chem. 51 (1984) 155.
52. Johnson, Ch. M., Shilton, M. G. and Howe, A. T., J. Solid State Chem. 37 (1981) 37.
53. Susic, M. V. and Minic, D. M., Solid State Ionics 6 (1982) 327.
54. Howe, A. T. and Shilton, M. G., J. Solid State Chem. 34 (1980) 149.
55. Kahil, H., Forestier, M. and Guitton, J., "Electrochemical Behavior of the Composite Electrode of MnO_2 -HUP-Acetylene Black" (in:) Solid State Protonic Conductors III -- for Fuel Cells and Sensors, Odense University Press, Denmark, 1985.
56. Krauer, K. D., Stall, I. and Rabenau, A., Solid State Ionics 9/10 (1983) 1061.

57. Ono, A., J. Mat. Sci. 19 (1984) 2691.
58. Perrino, C. T. and Wentreek, P., J. Solid State Chem. 10 (1974) 36.
59. Susic, M. V. and Minic, D. M., Solid State Ionics 2 (1981) 309.
60. Minic, D. M., Susic, M. V., Atanasoska, L. and Mioc, V. B., Solid State Ionics 14 (1984) 117.
61. Yamashita, K. and Nicholson, P. S., Solid State Ionics 20 (1986) 147.
62. Yamashita, K. and Nicholson, P. S., Solid State Ionics 20 (1985) 121.
63. Stephen, P.M.S. and Howe, A. T., Solid State Ionics 1, (1980), 461.
64. Yamamoto, O., Takeda, Y., Kanno, R. and Fushimi, M., Solid State Ionics 17 (1985) 107.
65. Chandra, S. and Singh, N., Solid State Ionics 9/10 (1983) 1067.
66. Barbes, H., Mascherpa, G., Fourcade, R. and Ducourant, B., J. Solid State Chem. 60 (1985) 95.
67. Ikawa, H., Tsurumi, T., Urabe, K. and Udagawa, S., Solid State Ionics 20 (1986) 1.
68. Tsurumi, T., Ikawa, H., Ishimori, M., Urabe, K. and Udagawa, S., Solid State Ionics 21 (1986) 31.
69. Tolpadi, S. K., Chandra, S. and Hashmi, S. A., Solid State Ionics 18/19 (1986) 1008.
70. Alberti, G., Bracardi, M. and Casciola, M., Solid State Ionics 7 (1982) 243.
71. Krogh Andersen, E., Krogh Andersen, I. G., Moeller, C. K., Simonsen, K. E. and Skou, E., Solid State Ionics 77 (1982) 301.
72. Alberti, G., Casciola, M., Constantino, V. and Leonardi, M., Solid State Ionics 14 (1984) 289.
73. England, W. A., Cross, M. G., Hamnett, A., Wiseman, P. J. and Goodenough, J. B., Solid State Ionics 77 (1982) 301.
74. Takahashi, T., Tanase, S. and Yamamoto, O., Electrochemistry Acta 23 (1978) 369.
75. Engstrom, H., Bates, J. B. and Boatner, T. A., J. Chem. Phys. 81 (1984) 2528.
76. Lee, W. K., Nowick, A. S. and Boatner, L. A., Solid State Ionics 18/19 (1986) 989.
77. Takahashi, T. and Iwahara, H., Res. Chim. Miner. 17 (1980) 243.

78. Uchida, H., Maeda, N. and Iwahara, H., Solid State Ionics 11 (1983) 117.
79. Mitsui, A., Miyayama, M. and Yanagida, H., Solid State Ionics 22 (1987) 213.
80. Bonanos, N., Ellis, B., and Mahmood, M. N., "Oxide Ion Conduction in Ytterbium-Doped Strontium Cerate," Solid State Ionics, 28/30, pp. 579-584 (1988).
81. Iwahara, H., Esaka, T., Uchida, H. and Maeda, N., Solid State Ionics, 3/4, pp. 359 (1981).
82. Iwahara, H., "High Temperature Proton Conducting Oxides and Their Applications to Solid Electrolyte Fuel Cells and Steam Electrolyzer for Hydrogen Production," Solid State Ionics, 28/30, pp. 573-578 (1988).
83. Scherban, T., Lee, W-K, and Nowick, A. S., in Yb-Doped SrCeO₃ and BaCeO₃, Solid State Ionics, 28/30, pp. 585-588 (1988).
84. Iwahara, H., Uchida, H. and Morimoto, K., "High Temperature C₁-Gas Fuel Cells Using Proton Conducting Solid Electrolytes," Extended Abstracts, Vol. 87-2, Electrochemical Society Fall Meeting, Honolulu, Hawaii, October 18-23, 1987, p. 266.
85. Yamamoto, O., Takeda, Y., Kanno, R. and Noda, N., Solid State Ionics 22 (1987) 241.
86. Kertesz, M., Riess, I., Tannhauser, D. S., Langpape, R. and Rohr, F. J., J. Solid State Chem. 42 (1982) 125.
87. Isenberg, A. O., Solid State Ionics 3/4 (1981) 431.
88. Ohno, Y., Nagata, S. and Sato, H., Solid State Ionics 3/4 (1981) 439.
89. Tedman, C. S., Jr., Spacil, H. S. and Mitoff, S. P., J. Electrochem. Soc. 116 (1969) 1170.
90. Isaac, H. S. and Olmer, L. J., J. Electrochem. Soc. 129 (1982) 436.
91. Werkerk, M. J., Mammink, M.W.J. and Brugraff, A. J., J. Electrochem. Soc. 130 (1983) 70.
92. Mizusaki, J., Amano, K., Yamauchi, S. and Fueki, K., Solid State Ionics 22 (1987) 313.
93. Mizusaki, J., Amano, K., Ymauchi, S. and Fueki, K., Solid State Ionics 22 91987) 327.
94. van Buren, F. R., Broers, G.J.H., Boesveld, C. and Bauman, A. J., J. Electroanal. Chem. 87 (1978) 381.
95. Fabry, P. and Kleitz, M., Electroanal. Chem. Interfacial Electrochem. 57 (1974) 165.

96. Yanagida, H., Brook, R. J. and Kroeger, F. A., J. Electrochem. Soc. 117 (1970) 200.
97. Tsotis, T. T., Sane, R. C., Webster, I. A. and Goddard, J. D., J. Catal. 101 (1986) 416.
98. Nakamura, T., Misono, M. and Yoneda, Y., J. Catal. 83 (1983) 83.
99. Rickert, H., Electrochemistry of Solids -- An Introduction. Springer Verlag, Berlin, 1982.
100. Wagner, C., Adv. Electrochem. Eng. Vol. 4, p. 40, Wiley, New York, 1966.
101. Goge, M., Letisse, G. and Goult, M., Solid State Ionics 9/10 (1983) 937.
102. Heyne, L., "Electrochemistry of Mixed Ionic-Electronic Conductors" (in:) Solid Electrolytes, S. Geller, ed., Springer Verlag, Berlin, 1977.
103. Yde-Andersen, S., Lundsgaard, J. S., Malling, J. and Jensen, J., Solid State Ionics 13 (1984) 81.
104. Choudary, G. B., Maiti, H. S. and Subbarao, E. C., "Defect Structure and Transport Properties" (in:) Solid Electrolytes and Their Applications, Subbarao, E. C., ed., Plenum Press, New York, 1978.
105. Greaves, G., Malsbury, A. M. and Thomas, M., Solid State Ionics 18/19 (1986) 763.
106. Raistrick, I. D., "Application of Impedance Spectroscopy to Materials," Ann. Rev. Mater. Sci. 16 (1986) 343.
107. Schouler, E.J.L., "Impedance Spectroscopy in Solid State Electrochemistry" (in:) Solid State Protonic Conductors III -- for Fuel Cells and Sensors. Odense University Press, Denmark, 1985.
108. Sluyters-Rehbach, M. and Sluyters, J. H., Comprehensive Treatise of Electrochemistry 9 (1984) 177.
109. Skou, E., Krogh Andersen, I. G., Simonson, K. E. and Krogh Andersen, E., Solid State Ionics 9/10 (1983) 1041.
110. Slade, R.C.T., Hardwick, A. and Dickens, P. G., Solid State Ionics 9/10 (1983) 1093.
111. Yamada, K., Murase, M. and Iwase, M., J. Appl. Electrochem. 16 (1986) 69.
112. Weppner, W., "Enhanced Ionic Motion in Solid Electrode Materials," Proc. of NATO Symp. on Materials for Advanced Batteries. Plenum Press, New York, 1980.
113. Cheetham, A. K., "Structural Studies on Nonstoichiometric Oxides Using X-Ray and Neutron Diffraction" (in:) Nonstoichiometric Oxides, Sorensen, O. T., ed., Academic Press, 1981.

114. Eyring, L., "Some Uses of High-Resolution Electron Microscopy in Solid State Chemistry" (in:) Solid State Chemistry: A Contemporary Overview, Advances in Chemistry Series 186, American Chemistry Society, Washington, 1980.
115. Dickens, P. G. and Hibble, S. J., Solid State Ionics 22 (1986) 69.
116. Murphy, D. W., Solid State Ionics 18/19 (1986) 847.
117. Whittingham, M. S., Prog. Solid State Chem. 12 (1978) 41.
118. Isenberg, A. O., Proc. Symp. on Electrode Materials and Processes for Energy Conversion and Storage, The Electrochemical Society, Princeton, 1977.
119. Feduska, Isenberg, A. O., Thin Film Battery/Fuel Cell Power Generating System, Westinghouse Electric Corp., Report C-1197-17, June 1980.
120. Yamazaki, Y. and Namikawa, T., Abstract No. 4096, Energy Report Abstracts 12 (1986) 69.
121. Gouet, M., Chappey, B. and Guillou, M., C.R. Acad. Sci. C 280 (1975) 1117.
122. Arakawa, T., Saito, A., Shiokawa, J., Bull. Chem. Soc. Jpn. 35 (1982) 2273.
123. Ray, A. K. and Subbarao, E. C., Technology (in:) Solid Electrolytes and Their Applications, E. C. Subbarao, ed., Plenum Press, New York (1978).
124. Isaacs, H. S., Proc. Symp. on Fuel Cell Technology Status and Applications Institute of Gas Technology, Chicago, 1982.
125. Thornton, J. A., J. Vac. Sci. Technol. A 4 (1986) 3059.
126. Dixit, P. and Vook, R. W., Appl. Surf. Sci. 24 (1985) 239.
127. Quere, Y. and Perrin, A., Mater. Lett. 3 (1985) 340.
128. Spaepen, F., Gleer, A. L., Kelton, K. F., and Bell, J. L., Rev. Sci. Instrum. 56 (1985) 1340.
129. Canaday, J. D., Wheat, T. A., Kuriakose, A. K. and Ahmad, A., Int. J. Hydrogen Energy 12 (1987) 151.
130. Wang, D. Y. and Nowick, A. S., J. Electrochem. Soc. 128 (1981) 55.
131. Braunshtein, D., Tannhauser, D. and Riess, I., J. Electrochem. Soc. 128 (1981) 82.
132. Perfilyev, M. V., Solid State Ionics 9/10 (1983) 765.
133. Miura, N., Ozawa, Y. and Yamazone, N., Denki Kagaku, 53, (1985) 338.

134. Uvarov, N. F., Haiteretdinov ande, E F., Boldyrev, V. V., J. Solid State Chem. 51, (1984) 59.
135. Karaseva, T. A., Ukr. Khim. Zh. 52, (1986) 570.
136. England, W. A., Goodenough, J. B. and Wiseman, P. J., J. Solid State Chem. 49 (1983) 289.
137. Goodenough, J. B., "Covalency Criterion for Localized Versus Collective Electrons in Oxides With the Perovskite Structure," J. App. Phys., 37, (1967) 1415.
138. Heyn, L., "Electrochemistry of Mixed Ionic-Electronic Conductors, (in:) "Solid Electrolytes," S. Geller, Ed., Topics in Applied Physics, Vol. 21, Springer-Verlag, Berlin, 1977.
139. Nakamura, T., "Crystal Systems and Lattice Constants of Perovskite-Type Compounds BaThO_3 and $\text{Ba}_2(\text{BaU})\text{O}_6$," Chemistry Letters (1974) 429.
140. Baruer, C. and Kristen, H., "Tetravalent Neodymium in Perovskites, Proc. XII Rare Earth Research Conference," Denver, Colorado, Ch.E. Lundin, Ed., Univ. of Denver (1976) 645.
141. Kahil, H., Forestier, M. and Guitton, J., "Electrochemical Behavior of the Composite Electrode j-MnO_2 -HUP-acetylene Black" (in:) Solid State Protonic Conductors III -- for Fuel Cells and Sensors, Odense University Press, Denmark, 1985.
142. Glasser, L., Chemical Reviews 75 (1975) 21.
143. Tamura, H., Yoneyama and Matsumoto, Y., "Physicochemical and Electrochemical Properties of Pervoskites" (in:) Electrodes of Conductive Metallic Oxides -- Part A. Studies in Physical and Theoretical Chemistry II, S. Trasatti, ed., Elsevier, Amsterdam, 1980.
144. Witner, E.R.S., J. Catal. 6 (1966) 35.
145. Hibbert, D. B. and Tseung, A.C.C., J. Electrochem. Soc. 125 (1978) 74.
146. Fierro, J.L.G. and Banda, J.F.G., Catal. Rev.-Sci. Eng. 28 (1986) 265.
147. More, R. J. and White, J., J. Mat. Sci. 9 (1974) 1393.
148. Samsonov, G. V., ed., "The Oxide Handbook," IFI/Plenum, New York, 1973.
149. Trasatti, S. and Lodi, G., "Properties of Conductive Transition Metal Oxides with Rutile Type Strucutre" (in:) Electrodes of Conductive Metallic Oxides -- Part A. Studies in Physical and Theoretical Chemistry II, Trasatti, S., ed., Elsevier, Amsterdam, 1980.
150. Tarasevich, M. R. and Efremov, B. N., "Properties of Spinel-Type Oxide Electrodes" (in.) Electrodes of Conductive Metallic Oxides -- Part A. Studies in Physical and Theoretical Chemistry II, S. Trasatti, ed., Elsevier, Amsterdam, 1980.

151. Griva, A. P., Nikisha, V. V., Shelimov, B. N. and Kazanski, V. B., Kinet. Katal. 15 (1974) 104.
152. Boreskov, G. K., Borisov, Yu. A., Bulgakov, N. N., Muzykantov, V. S., Panov, G. I. and Tayrulnikov, P. G., Kinet. Katal. 16 (1975) 1246.
153. Muzykantov, V. S., Popovskii, V. V., Boreskov, G. K., Panov, G. I. and Skhrabina, R. A., Kinet. Katal. 13 (1972) 185.
154. Popovskii, V. V., Boreskov, G. K., Dzeventsii, Z., Muzykantov, V. S. and Shulmeister, T. T., Kinet. Katal. 12 (1971) 979
155. Andrushkevich, T. V., Boreskov, G. K., Popovskii, V. V., Muzykantov, V. S., Kimkhai D. M. and Sazonov, V. A., Kinet. Katal. 9 (1968) 595.
156. Tannhauser, D. S., Kilner, J. A. and Stelle, B.C.H., Nucl. Instr. Meth. Phys. Res. 218 (1983) 504.
157. Fierro, J.L.G., Tascon, J.M.D. and Tejuca, L. G., J. Catal. 89 (1984) 209.
158. Fierro, J.L.G. and Tajua, I. G., J. Catal. 85 (1984) 126.
159. Fierro, J.L.G., Tascon, J.M.D. and Tejuca, L. G., J. Catal. 93 (1985) 83.
160. Jacobson, A. J., Lewandowski, J. T. and Johnson, J. W., J. Less-Common Metals 116 (1986) 137.
161. Chen, L., Liu, Y. and Chen, Y., J. Solid State Chem. 68 (1987) 132.
162. Chen, L., Liu, Y. and Chen, Y., J. Solid State Chem. 68 (1987) 128.
163. Iwahara, H., Uchida, H. and Morimoto, K., J. Electrochem. Soc. 137 (1990) 462.
164. Sammells, A. F., Visco, S. J. and Worrell, W. L., Proceedings of the EPRI/GRI Fuel Cell Workshop, Orlando, Florida, October 26-27, 1989.

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