

# FUEL CELL

Preliminary  
Program

1992  
Fuel  
Cell  
Seminar

November 29—December 2, 1992  
Tucson, Arizona

In Cooperation with

**UNITED STATES**  
Department of Energy  
Electric Power Research Institute  
Gas Research Institute  
National Aeronautics and Space Administration

**EUROPE**  
Commission of the European Communities

**JAPAN**  
Fuel Cell Development Information Center

Sponsored by  
the Fuel Cell  
Seminar  
Organizing  
Committee

Wednesday, December 2, PM (Cont'd)

**Thin Film Electrolytes for Intermediate Temperature SOFC Applications**

C. Chen, M. Nasrallah and H. Anderson, University of Missouri-Rolla

**A Mathematical Model of a Tubular Solid Oxide Fuel Cell**

W. Wepfer and N. Bessette II, Georgia Institute of Technology

**Testing a Multi-kWe SOFC Power Generation System**

J. Makiel, L. Shockling, T. Fabis, Westinghouse Electric Corporation

**Westinghouse SOFC Field Unit Experience — Update**

S. Veyo, Westinghouse Electric Corporation

**Advances in MSOFC Systems and Technology**

R. Gibson, N. Minh, L. Schipper and T. Armstrong, Allied-Signal Aerospace Company

**Modeling of Planar Solid Oxide Fuel Cells**

J. Hartvigsen, S. Elangovan and A. Khandkar, Ceramtec, Inc.

**RESEARCH TOPICS (8D)**

**Synthesis and Characterization of Protonic Conductors**

D. Stevenson, N. Jiang, F. Henn, R. Buchanan, Z. Lu and X. Wang, Stanford University, R. Hiskes and S. DiCarolis, Hewlett Packard Laboratories

**Optimal Design and Long-term Performance Limits for High-Power Density MCFC Electrodes: Current Technology and Projected Advances**

J. Selman, Illinois Institute of Technology

**Direct Internal Reforming in SOFC Anodes: Modeling Analysis**

J. Selman and Y. Hsiao, Illinois Institute of Technology

**Electrochemical Corrosion Studies of Fe-Based Ni and Fe-Based Cr Alloys in Molten Carbonates**

I. Uchida, and T. Nishina, Tohoku University

**Study on the Interfacial Characteristics of Porous Nickel Electrode for Molten Carbonate Fuel Cell by Means of Electrochemical Impedance Spectroscopy**

L. Giorgi, E. Simonetti and A. Pozio, ENEA

Wednesday, December 2, PM (Cont'd)

**Metal Wettability Behavior by Molten Carbonate**

T. Watanabe and J. Selman, Illinois Institute of Technology

**LiFeO<sub>2</sub> as a Cathode Material in Carbonate Fuel Cells: Solubilities and Oxygen Reduction Kinetics**

D. Shores, Y. Qu and R. Atanasoski, University of Minnesota

**Effects of Composition on Sintering of Chromite Current Interconnects in SOFC**

L. Chick, J. Bates, G. Maupin, Pacific Northwest Laboratory, and M. Etchemendy, NORCUS

**Influence of Anodic Materials Preparation and Processing on CH<sub>4</sub> Steam Reforming Reaction for Internal Reforming SOFC**

L. Zanibelli, C. Perego, C. Flego, G. Piro and F. Gagliardi, Eniricerche S.p.A.

**Studies on the Perovskite Cathode for the Molten Carbonate Fuel Cell**

H. Chun, J. Lim, K. Park, K. Kim, Korea University, and J. Lee, University of Pusan

**MODELING AND PROGRAM TOPICS (8E)**

**Naval Propulsion Direct Fuel Cell Advancements Using Diesel Fuel**

W. Kumm, Arctic Energies, Ltd.

**Potential Polar Power Systems with Practical Fuel Cells**

H. Lisle, Jr. and W. Kumm, Arctic Energies, Ltd.

**Fuel Cells and Their Strategic Importance — A Case Study of a Technological Breakthrough?**

I. Stann, State Energy Commission of Western Australia

**Molten Carbonate Fuel Cell Cogeneration Plant in Sweden — A Technical and Economical Feasibility Study**

A. Bengtsson, N. Carstedt, Vattenfall Energisystem AB, and L. Spante, Vattenfall Utveckling AB

**SCAQMD Air Quality Regulations and Fuel Cells**

R. George, South Coast Air Quality Management District (SCAQMD)

12 Noon-2:30 pm

Noon-1 pm

STUDY ON THE INTERFACIAL CHARACTERISTICS OF POROUS  
NICKEL ELECTRODE FOR MOLTEN CARBONATE FUEL CELL BY MEANS  
OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

L. Giorgi, E. Simonetti and A. Pozio  
ENEA - C.R.E. Casaccia  
Division of Electrochemical Technologies and Plants  
Via Anguillarese n. 301  
00060 S. Maria di Galeria (Rome), Italy

The kinetics of gas electrode reactions in molten carbonate are very important to understand the electrode processes in the MCFC. The experimental difficulties related to working in molten carbonate systems have restricted the evaluation of kinetic data to submerged flat electrodes in excess of electrolyte. The conditions of a porous gas diffusion electrode are quite different and it is important to verify the validity of the kinetic parameters also in these conditions.

The cathodic process ( $1/2O_2 + CO_2 + 2e^- \rightleftharpoons CO_3^{2-}$ ) has been extensively studied and many approaches have been utilized in the past, in order to establish the r.d.s. and to obtain the numeric values of the reaction orders relative to  $O_2$  and  $CO_2$ .

The results reported in literature, both on flat [1,2] and porous [3,4] electrodes, are contradictory and the reaction mechanism for  $O_2$  reduction in molten carbonates is not well understood.

The aim of the present paper is to investigate the porous nickel electrode/molten carbonates interface, in the case of an in situ lithiated nickel oxide electrode, by means of electrochemical impedance spectroscopy (EIS).

#### EXPERIMENTAL

A symmetrical cell, made of recrystallized alumina, was assembled using two cathodes instead of a cathode and an anode. The electrodes were two identical porous Ni disks (geometric area  $3 \text{ cm}^2$ , porosity  $75 \pm 5\%$ , mean pore size  $4 \pm 1 \mu\text{m}$ ). The tile was  $48\%_w \gamma\text{-LiAlO}_2$  and  $52\%_w$  lithium/potassium carbonate mixture ( $\text{Li/K} = 62/38 \text{ \%mol}$ ).

The cell was operated at  $650 \pm 2 \text{ }^\circ\text{C}$  and fed with a  $CO_2/O_2$  mixture at variable composition.

A potentiostat-galvanostat Solartron mod.1286 and a FRA Solartron mod.1250, both controlled by a HP mod.310

computer, were used to perform the EIS measurements. The cell was polarized at  $i=0$ , with a superimposed sinusoidal signal ( $236 \mu\text{A}/\text{cm}^2$ ), in the frequency range from 0.1 Hz to 65 kHz.

#### SPECTRA ANALYSIS

A typical EIS spectrum at  $650^\circ\text{C}$  ( $p\text{O}_2=0.14 \text{ atm}$ ,  $p\text{CO}_2=0.30 \text{ atm}$ ) is shown in fig.1. At a first look the spectrum is clearly depressed, due to the porous electrode structure. This phenomenon depends on gas composition: at  $p\text{CO}_2 < 0.3 \text{ atm}$ , whatever is the  $p\text{O}_2$ , the depression angle value is so that the impedance phase angle is less than the theoretical value of  $22.5^\circ$  for a porous electrode [5]. Such a condition is verified for  $\delta^2\omega/D < 10$ , where  $\delta$  is the electrolyte thickness,  $\omega$  the angular frequency and  $D$  the diffusion coefficient of reacting species. This inequality is only true when a very thin electrolyte layer is present [6].

Starting from this point of view, the equivalent electrical circuit for the cathode/electrolyte interface can be simulated by a network made up with a charge transfer resistance, a double layer capacitance and a characteristic element of a system in which is present a finite diffusion layer:

$$(1) \quad Z_0(\omega) = \tanh [B(j\omega)^{0.5}] / [Y^0(j\omega)^{0.5}]$$

in which  $\omega$  is the angular frequency,  $B$  and  $Y^0$  are two parameters containing the diffusion coefficient of the reactant species and the film thickness.

The presence of a  $Z_0$  element is a confirmation that the pores of the cathode are not completely flooded: the pore walls are coated by a thin film of electrolyte and the concentration gradient of active species extends completely to the film thickness.

At constant  $p\text{CO}_2$ , as  $p\text{O}_2$  increases, both the total real part of impedance ( $R_p$ ) and the maximum of the imaginary part of impedance ( $Z_{\text{Im}_{\text{max}}}$ ) decrease. On the contrary when  $p\text{O}_2$  is constant, as  $p\text{CO}_2$  increases, both  $R_p$  and  $Z_{\text{Im}_{\text{max}}}$  increase. As a consequence it can be concluded that: the  $p\text{O}_2$  has a positive influence on the cathodic reaction, while the  $p\text{CO}_2$  has a negative influence. These results agree with the mechanisms proposed in literature [1,2,3,4]:

$$(2a) \quad \text{POP} \quad i_0 = k p\text{O}_2^{0.375} p\text{CO}_2^{-1.25}$$

$$(2b) \quad \text{SOP} \quad i_0 = k p\text{O}_2^{0.625} p\text{CO}_2^{-0.75}$$

$$(2c) \quad \text{POMCP} \quad i_0 = k p\text{O}_2^{0.375} p\text{CO}_2^{-0.25}$$

in which POP, SOP and POMCP means, respectively, peroxide path, superoxide path and peroximonocarbonate path.

## ACTIVATION ENERGIES

Several parameters can be easily extract from the spectra: electrolyte conductivity ( $\sigma$ ), total polarization resistance ( $R_p$ ), maximum imaginary component of impedance ( $-Z_{Im_{max}}$ ) and frequency ( $f_{max}$ ) of  $-Z_{Im_{max}}$ . All these parameters are thermally activated according to an Arrhenius type equation. The activation energies are summarized in Table I, from which it is clear that  $\sigma$  and  $f_{max}$  are relative to exothermic phenomena, while  $R_p$  and  $Z_{Im_{max}}$  are relative to endothermic processes.

The negative dependence of  $R_p$  from temperature points out an increase in charge transfer and diffusion rate. Nevertheless, it is difficult to split the influence of the single processes on the overall phenomenon.

The same behaviour is shown by  $-Z_{Im_{max}}$ . The physical meaning of such a parameter is difficult to explain, also if Yuh [3] tried to use it to determine the reaction orders of  $O_2/CO_2$  reduction.

The  $f_{max}$  is inversely related to the system time constant, therefore the electrodic processes are accelerated by temperature.

## CHARGE TRANSFER RESISTANCE AND REACTION ORDERS

The spectra can be subdivided in two regions: the low-medium frequency one dominated by diffusion and the high frequency one in which the kinetic aspect is prevalent.

Using a fitting procedure [7] it was possible to obtain the equivalent circuit shown in fig.2; a good correlation between the high frequency resistance ( $R_{hf}$ ) and partial gas pressures was found. That means the  $R_{hf}$  can be associated to the charge transfer resistance  $R_{ct}$ . In the case of porous electrodes the relationship between  $R_{ct}$  and  $R_{hf}$  is expressed by:

$$(3) \quad R_{hf}^{0.5} \approx R_{ct}$$

and

$$(4) \quad 1/R_{ct}^2 \approx p_{O_2}^a p_{CO_2}^b$$

Keeping constant the partial pressure of a gas, it is possible to derive the reaction order relative to the other gas:

$$(5a) \quad \log R_{hf} = -1/2 \log k' - a/2 \log p_{O_2}$$

$$(5b) \quad \log R_{hf} = -1/2 \log k'' - b/2 \log p_{CO_2}$$

Therefore from the slope of the previous equations it is possible to draw out the reaction orders.

The reaction orders calculated from different series of measurements, made on two different cells, are shown in Table II.

The mean calculated reaction orders are:  $a=0.37\pm 0.09$  and  $b=-1.34\pm 0.19$ . These results are in good agreement with the theoretical values for the peroxide mechanism, especially in the case of oxygen reaction order.

## REFERENCES

1. A.J. Appleby, S.B. Nicholson, "Reduction of oxygen on silver electrodes in ternary in alkali carbonate melts", J. Electroanal. Chem, Vol.83, p.759, 1980.
2. I. Uchida, T. Nishina, Y. Mugikura, K. Itaya, "Gas electrode reactions in molten carbonate media", J. Electroanal. Chem., Vol.206, p.229, 1986.
3. C.Y. Yuh, J.R. Selman, "The polarization of molten carbonate fuel cell electrodes-II. Characterization by AC impedance and response to current interruption", J. Electrochem. Soc., Vol.138, p.3649, 1992.
4. T. Nishina, G. Lindbergh, T. Kudi, I. Uchida, "Electrode kinetics and modeling of oxygen reduction in molten carbonate media", Proc. of International Fuel Cell Conference, p.193, 3÷6 February, 1992, Makuhari (Japan).
5. R. de Levie, L. Pospisil, "On the coupling of interfacial and diffusional impedances, and the equivalent circuit of an electrochemical cell", J. Electroanal. Chem, Vol.22, p.277, 1969.
6. A. Pozio, Thesis, University of Rome, December, 1991.
7. L. Giorgi, E. Simonetti, A. Pozio, "Electrode kinetics of oxygen reduction on porous nickel carbonate melt", Proceeding of 2nd International Symposium on Electrochemical Impedance Spectroscopy, 11÷17 July, 1992, S. Barbara (USA).

Table I - Activation energies obtained from EIS spectra.

Parameter	$E_{act}$ (kJ/mol)
$\sigma$	$38\pm 2$
$R_p$	$-94\pm 5$
$-Z_{Im_{max}}$	$-88\pm 3$
$f_{max}$	$208\pm 17$

Table II - Reaction orders calculated from EIS data.

$pO_2$ (atm)	$pCO_2$ (atm)	a	b	r
0.10÷0.60	0.10	$0.30 \pm 0.08$		0.96
0.05÷0.65	0.30	$0.36 \pm 0.09$		0.91
0.10÷0.60	0.30	$0.44 \pm 0.08$		0.94
0.14	0.10÷0.60		$-1.37 \pm 0.23$	0.95
0.14	0.05÷0.65		$-1.28 \pm 0.20$	0.97
0.50	0.05÷0.50		$-1.38 \pm 0.14$	0.98

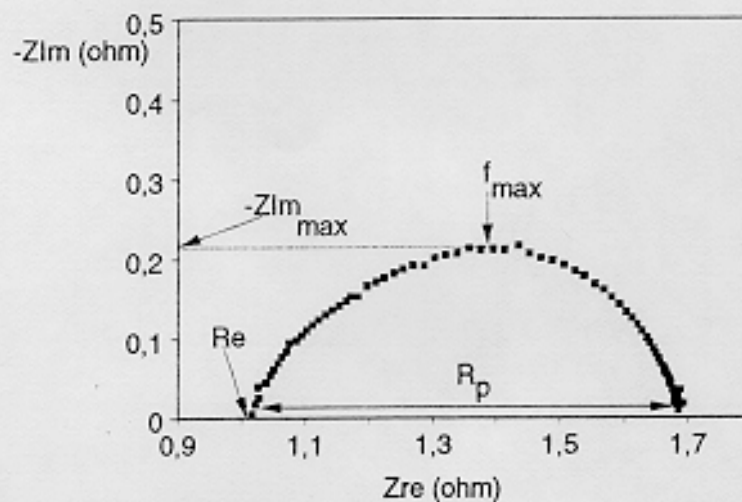


Fig.1 - Typical NiO(Li) EIS spectra in molten carbonates.

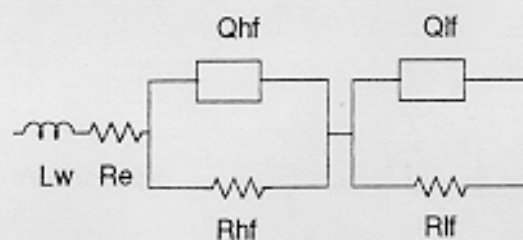


Fig.2 - Equivalent electrical circuit for the EIS data of fig.1.

[Lw: wire's inductance, Re: electrolyte resistance, R: high (hf) and low (lf) resistance, Q: high (hf) and low (lf) constant phase element]