

EVALUATION OF POROUS CERAMIC CATHODE LAYERS
FOR SOLID OXIDE FUEL CELLS

L.G.J. de Haart, K.J. de Vries
University of Twente, P.O. Box 217,
7500 AE Enschede, the Netherlands

A.P.M. Carvalho, J.R. Frade, F.M.B. Marques
Universidade de Aveiro, 3800 Aveiro, Portugal

(Received February 20, 1991; Communicated by A.W. West)

ABSTRACT

$\text{Sr}_{0.15}\text{La}_{0.85}\text{MnO}_3$ layers with 2 and 10 μm thickness, deposited on zirconia based electrolytes, were evaluated as cathodes for high temperature applications. Different electrode layers were characterized in terms of thickness, porosity, three phase boundary line per unit area (TPBL), and concentration polarization behavior. Electrodes with maximum porosity and TPBL exhibit minimum concentration polarization losses at constant current density.

MATERIALS INDEX: lanthanum, manganese, platinum, zirconia

Introduction

The development of technological applications based on ionic transport properties of zirconia electrolytes is strongly dependent on the successful development of different components for such applications. Noble metal electrodes like Pt, used for many years in laboratory experiments, are not acceptable for technological applications due to their high cost. Ceramic electrode materials are an interesting alternative if they can meet some specific requirements. For Solid Oxide Fuel Cells (SOFC) or Steam Electrolyzers (SE) they must have high electrical conductivities, adequate catalytic properties, long term stability, and physical and chemical compatibility with the electrolyte. The first criterion is of great importance for these current carrying devices to reduce ohmic losses and ensure optimum economical performance. The remaining requirements are still valid for open circuit applications like oxygen sensors.

In recent years, a large effort has been made to identify the optimum combination of properties in perovskites based on LaCoO_3 or LaMnO_3 doped with Sr or Ca. While the highest electrical conductivities were found for the Co based materials [1-3], the perovskites based on LaMnO_3 exhibit better stability towards the electrolyte and thermal expansion coefficients reasonably similar to yttria stabilized zirconia (YSZ) [1,4]. Some of these materials were already evaluated as cathode materials for SOFC, with very promising results [4].

Polarization measurements performed with point type electrodes are quite useful in order to identify the relative behavior of different materials, but extrapolation of results for actual electrode layers is not straightforward. Electrode morphology is expected to be of fundamental importance in determining polarization losses [1,5]. To obtain minimum ohmic losses with a constant layer thickness, electrode layers should have small porosity. However, dense electrode layers with minimum porosity will block gas phase mass transport, resulting in high concentration polarization losses. For porous electrode layers the electrode morphology determines the extent of the three phase boundary line per unit area (TPBL), where electrode, electrolyte and gas phase are in contact. Optimum performance is expected for electrode layers with the largest TPBL at constant porosity. In the past the influence of these parameters on the behavior of noble metal electrodes has been studied [6]. However, in this case working temperatures were usually low to avoid changes on electrode morphology due to metal sintering. Little information is available on these aspects for ceramic electrodes. The present research was conceived to evaluate the role of different morphological aspects of Sr-doped LaMnO_3 (SLM) cathode layers on concentration polarization contribution.

Economical aspects are also of fundamental importance when selecting deposition techniques for large scale production. Filcoating is a well developed technique that meets these criteria. In previous work the appropriateness of this technique to produce layers with controlled thickness and morphology has already been demonstrated [7]. This deposition process and $\text{Sr}_{0.15}\text{La}_{0.85}\text{MnO}_3$, one of the ceramic materials that exhibits some of the above mentioned requirements for a SOFC cathode, were selected for the present research for these reasons.

Experimental Procedure

SLM materials were prepared following a citrate synthesis route [8]. XRD patterns agreed with results mentioned in literature [9]. Grain size separation was obtained by centrifuging suspensions of LSM powder in isopropyl alcohol. Different suspensions were prepared starting from powders with different grains size distributions. These suspensions were used in the deposition technique. The substrates were disks of YSZ, with about 13 mm diameter and 1 mm thick, prepared from commercially available YSZ powder (Zircar, ZrO_2 -12 wt% Y_2O_3). The YSZ substrates were polished with diamond paste, ultrasonically

cleaned in isopropyl alcohol and degreased in boiling hexane, prior to layer deposition. Then the YSZ substrates were immersed in the SLM suspensions and withdrawn at a constant speed. Layer thickness could be controlled by varying the withdrawal speed and the number of successive dips, while the layer morphology was strongly affected by the starting powder grain size distribution. After drying, layers were fired in order to achieve good mechanical stability and adhesion to the electrolyte. A detailed description of the deposition technique can be found elsewhere [7]. In the present work, electrode layers characterization was mostly based on SEM observations of cross sections (for thickness evaluation) and layer morphology.

Concentration polarization experiments were performed on YSZ disks with SLM electrodes deposited on one side of the cell and porous platinum electrodes deposited on the other side. The electroded disks were sealed against an impervious alumina tube with a Pyrex glass seal. A nitrogen stream was forced inside this alumina tube in order to contact with the SLM cathode, while the Pt electrode was kept in contact with air. The open circuit emf of the cell was used as a measure of the oxygen content in the streaming nitrogen, assuming that the Nernst Law was obeyed. With proper electrical connections, a d.c. source was used to impose different voltages to the cell. Under closed circuit conditions both cell voltage and current intensity were recorded. The experimental setup is schematically shown in Figure 1. The ceramic electrodes were connected to the Pt current collector by a painted Pt grid, to ensure nearly uniform current density throughout the electrode cross section.

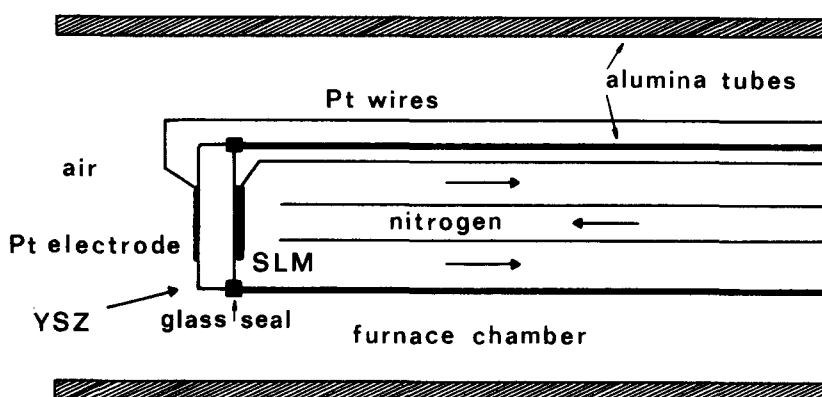


FIG. 1
Schematic representation of the experimental setup

Results and Discussion

Cathode layer morphology

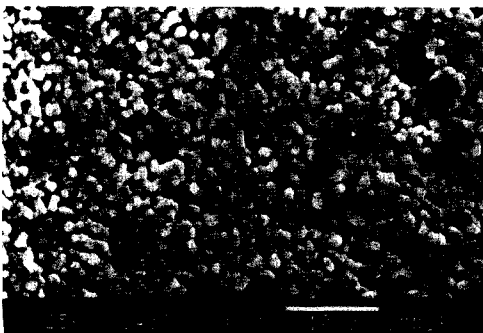
SLM layers with 2 and 10 μm thickness presented the typical characteristics described in Table I for specimen A and B, as determined from SEM photos using point counting and the line intercept method [10]. A porous Pt layer was analyzed for comparison and the results are also included in Table I. Concentration polarization measurements performed on cells with these electrode layers are reported in the next section.

TABLE I

Electrode Layer Characterization

Specimen\ thickness (μm)	Electrolyte uncovered area (%)	Three-phase bound. line (mm/mm^2)	Avg. pore diameter (μm)
A \ 2	29%	8.9×10^2	1.6
B \ 10	<5%	<40	≈ 2
Pt \ 3	42%	3.3×10^2	not applicable

Data included in Table I show that layer A is slightly better than the porous Pt electrode in what concerns to the TPBL, although the electrolyte uncovered area is smaller for the ceramic electrodes. Electrode layer B exhibits the worst results in terms of both TPBL and electrolyte uncovered area. The differences between layers A and B can be qualitatively understood from SEM micrographs (Figures 2 and 3).



(a)



(b)

FIG. 2

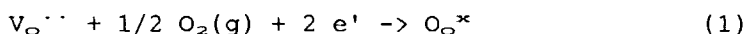
Micrograph of SLM layer A: (a) top view; (b) cross section.



FIG. 3
Micrograph of SLM layer B: (a) top view; (b) cross section.

Concentration polarization measurements

At 1000°C zirconia based electrolytes such as YSZ are pure ionic conductors for oxygen pressures ranging from ambient pressure to less than 10^{-15} Pa [11]. In such conditions, a voltage V applied to the electrolyte results in electrochemical transport of oxygen through the material. The mobile ionic defects are oxygen vacancies and cathodic reduction of oxygen requires the reaction of an oxygen atom with two electrons and one oxygen vacancy. The actual sequence of steps in this reaction depends on different parameters (working conditions, materials characteristics, etc.) but the overall cathodic reaction can be described by:



using the Kroger-Vink notation. Accordingly, $V_{O}^{\bullet\bullet}$ corresponds to a fully ionized oxygen vacancy, e' represents one electron, O_{O}^{\times} an oxygen ion on its regular lattice position, and O_2 an oxygen molecule in the gas phase. The usual assumptions are that oxygen is supplied by the atmosphere, oxygen vacancies are present in the electrolyte, and electrons are supplied by the electrode material. Therefore the reaction must take place near the TPBL, where electrode, electrolyte and gas phase are in contact, as the concentration and mobility of each species participating in the reaction is usually small except in one of these phases.

Oxygen supply to the reaction sites requires oxygen transport from the gas phase. The driving force for oxygen transport in gas phase is the oxygen pressure gradient. Assuming unidirectional transport, from Fick's diffusion law and Faraday's law it can be shown that the current density in the cell (J) is related to the oxygen pressure gradient in the gas phase (dP/dx) by:

$$J = (4FD/RT) \, dP/dx \quad (2)$$

Insufficient supply of oxygen results in local drop in the oxygen partial pressure at the gas/electrolyte interface, causing an increase in the driving force for oxygen diffusion in the gas phase. This increase in the driving force for oxygen supply leads to an increase in concentration overpotential. The maximum flux of oxygen in the gas phase and the corresponding limiting current density (J_L) will be proportional to the oxygen partial pressure in the streaming gas (P) [12]:

$$J_L = (4FD/RT) \cdot (P/\delta_e) \quad (3)$$

In this expression δ_e corresponds to the equivalent boundary layer thickness, where the drop in oxygen partial pressure occurs, D corresponds to the oxygen diffusion coefficient in the gas mixture, T is the absolute temperature, and R and F have their usual significance. For a well defined electrode and typical working conditions, the cathodic concentration overpotential (η_c) depends on the current density as [12]:

$$\eta_c = - (RT/4F) \cdot \ln (1-J/J_L) \quad (4)$$

From this equation it can be concluded that as the current density approaches the limiting value J_L , the concentration overpotential becomes increasingly important.

The parameter δ_e , introduced in eq. (3), should not be identified as the electrode layer thickness. Actually, δ_e corresponds to the sum of different resistances to gas phase oxygen transport. These contributions include the resistance to the transport process of oxygen outside the electrode pores, which strongly depends on the gas flow rate, and the resistance to oxygen transport inside the electrode pores, which depends on electrode characteristics. With reasonably high gas flow rates the former contribution becomes negligible, and δ_e will depend mostly on electrode thickness, porosity, and morphological characteristics [5]. In these circumstances, for constant temperature, gas flow rate, and oxygen partial pressure, δ_e conveniently describes the electrode behavior in terms of resistance to gas phase mass transport. From eq.s (3) and (4) it can be seen that large values of δ_e (or small limiting current densities) indicate that one electrode will originate high concentration polarization losses, while for small values of δ_e (large limiting current densities), concentration polarization losses will become small.

Polarization measurements performed in this work have used this approach to characterize different cathode layers. The applied voltage to the cell was increased until mass transport limiting conditions were reached. A simple cell with two electrodes is enough to obtain the relevant information: the oxygen content in the flowing gas mixture and the corresponding limiting current densities. Different oxygen contents in the streaming nitrogen were imposed to identify the electrode behavior in a range of oxygen pressures.

Figure 4 includes two typical curves relating the cell current density (J) to the applied voltage (V_p) corrected for the open circuit electromotive force (V_o), in order to ensure that the curve starts at the origin. In this figure, curve b corresponds to the Pt electrode while curve a represents the SLM electrode layer B. One interesting observation is that both curves deviate from ohmic behavior in different ways. While for the Pt electrode deviation increases progressively with applied voltage, for the SLM electrode the curve exhibits an inflection point. This behavior may be the result of changes in electrode kinetics when the SLM layer is cathodically polarized. It has already been suggested that under cathodic polarization SLM oxygen vacancies participate directly in the cathodic reaction [13]. This fact would result in an increasingly large surface area for cathodic reaction with increasingly high cathodic polarization. In this manner the increase in concentration polarization with increasing current density might be temporarily sustained by the increase in reaction surface area. This would indicate that limiting current densities obtained in this manner are overestimated in terms of actual behavior for SOFC operation where air is present and smaller cathodic concentration overpotentials are expected.

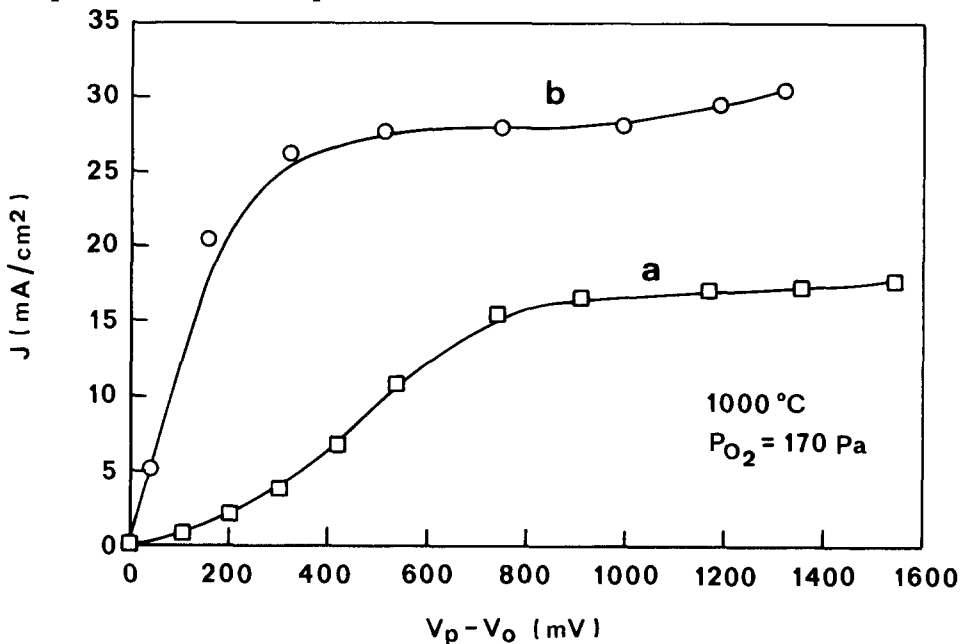


FIG. 4

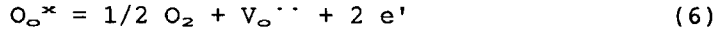
Current density versus applied voltage (V_p), corrected for the open circuit emf (V_o), for SLM layer B (a) and Pt (b).

The role of cathodic concentration overpotentials on electrode process can be explained on the basis of a relatively simple model. Previous work suggests that Schottky defects are the dominant ionic defects in SLM [13]. The increase in electronic conductivity with increasing strontium content seems

to indicate that the concentration of electronic charge carriers is determined by the dopant concentration. The usual assumption is that in air these carriers are small polarons localized on manganese ions. Using the Kroger-Vink notation, the simplified electroneutrality condition describing this situation reduces to:

$$[\text{Sr}_{\text{La}}'] = [\text{Mn}^{\cdot\cdot}] \quad (5)$$

and defect reactions to be considered in this treatment are:



$$0 = e' + h^{\cdot} \quad (7)$$



From equilibrium constants corresponding to reactions (6), (7) and (8), together with eq. (5), it can be shown that:

$$[\text{V}_\text{O}^{\cdot\cdot}] \propto \text{Po}_2^{-1/2} \quad (9)$$

The ionic transport number (t_1) of SLM, although small, is the usual ratio of ionic (σ_1) to total conductivity (σ_e):

$$t_1 = \sigma_1 / \sigma_e \quad (10)$$

For values of ionic conductivity much smaller than the values of electronic conductivity (σ_e), eq. (10) can be expressed as:

$$t_1 \approx \sigma_1 / \sigma_e \quad (11)$$

As the conductivity components correspond to the product of defect concentration, mobility, and charge, based on eq.s (5) and (9), and assuming that defect mobilities are independent of oxygen partial pressure, it can be shown that t_1 will be proportional to $\text{Po}_2^{-1/2}$. An interesting way to emphasize the role of concentration overpotential on the electrode material transport properties is to determine the ratio of the ionic transport numbers corresponding to the extreme oxygen pressure conditions in contact with the electrode material. This can be given as:

$$t_{1,\text{TPBL}} / t_1 = (P / P_{\text{TPBL}})^{1/2} \quad (12)$$

where P_{TPBL} and $t_{1,\text{TPBL}}$ are the oxygen partial pressure and ionic transport number of the electrode material in the TPBL, and P and t_1 the corresponding values in the streaming gas. The same ratio can be related to the concentration overpotential through the Nernst relation, which results in:

$$t_{1,\text{TPBL}} / t_1 = \exp(2F\eta_c / RT) \quad (13)$$

Noticing that the cathodic overpotential (as expressed in eq. (4)) is a positive quantity, it becomes obvious that the ionic transport number of SLM exhibits a strong increase with increasing concentration overpotential. This also means that a significant concentration of oxygen vacancies will be available

in the electrode material, to participate in the electrode reaction. However, from the gas phase oxygen pressure profiles obtained from the solution of Fick's diffusion law, even when J/J_L approaches 1, it can be shown that only a small portion of the electrode material near the TPBL will exhibit a significant increase in ionic transport number.

Figure 5 shows the results obtained with the polarization experiments in a plot of limiting current density versus oxygen partial pressure. These data indicate that limiting current densities are proportional to the oxygen content in the gas phase. The correlation factors are somewhat poor (0.98) for all cases. The dependence in Figure 5 is coherent with the fundamental assumption that gas phase oxygen transport is the rate limiting step for the present working conditions [5,12,14]. The results presented in Figure 5 also indicate that cathodic limiting current densities for electrode A are smaller than those obtained for Pt electrodes, and that cathodic limiting current densities for electrode B are even smaller. Considering the previously mentioned arguments on the increase in active surface area for cathodic reaction with cathodic polarization of SLM layers, and comparing the behavior of both SLM layers, it must be concluded that the increase in active surface area for cathodic reaction is not enough to compensate for inadequate morphology. This means that although a second mechanism for cathodic reaction might be operating for high cathodic overpotentials, the actual contributions in terms of ionic transport are not very large. This result is also coherent with the model previously discussed.

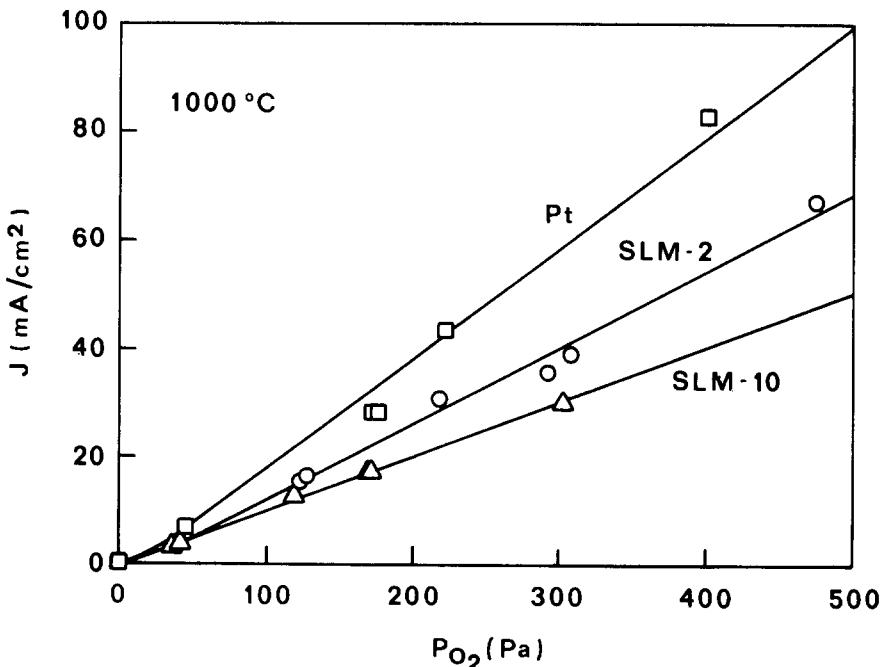


FIG. 5

Cathodic limiting current densities obtained with different electrode layers (see Table I).

The boundary layer thickness, estimated from present data on the basis of equation (3), is three orders of magnitude larger than the corresponding electrode thickness. As large pores are present in all electrode layers, and the overall porosity is not negligible, the existence of a constriction resistance related to the electrode/electrolyte effective surface area that participates in the electrode process could explain this type of result. In these circumstances the blocking characteristics of any electrode layer would be a combined result of electrode thickness, porosity, and TPBL. This can explain why the Pt electrode with a smaller TPBL and larger porosity exhibits a better performance than the SLM layer A with larger TPBL and smaller porosity. In terms of comparing SLM layers A and B, the decrease in TPBL and porosity resulted in smaller limiting current densities, as expected. This general explanation also agrees with the cathodic overpotential dependence on electrode layer thickness (0.8 to 3.2 μm) reported by Yamamoto et al. [1], who found minimum overpotentials at 0.1 A/cm² for layers with 2 μm thickness, in air at 800°C. These polarization measurements performed in working conditions where concentration polarization is unlikely to be dominant indicate that electrode morphology is also important in terms of activation polarization. The idea of constriction resistance is also valid in this case as a small TPBL will result in high local effective current densities and correspondingly high activation overpotentials.

Limiting current densities extrapolated on the basis of eq. (3) for air (21% oxygen content in the streaming gas) indicate that the limiting current densities for the Pt electrode would be about 4 A/cm². Only half this value would be obtained for electrode layer B. Estimates based on these values, eq. (4), and for current densities of 500 mA/cm², indicate that in air concentration overpotential would range from 3 mV for Pt to 8 mV for SLM layer B. Although these values are almost negligible it should be noticed that actual electrodes for SOFCs are expected to be much thicker, which means that electrode morphology must be carefully controlled in order to ensure low concentration polarization losses in this type of technological applications.

Conclusions

One painted Pt electrode and two SLM layers deposited by filmcoating with different characteristics behaved differently in terms of concentration polarization. Layers with higher TPBL and porosity exhibit minimum concentration polarization losses, while layers with minimum TPBL and low porosities exhibit large polarization losses. Electrode morphology will play a significant role in determining polarization losses in current carrying devices where large current densities are expected for operating conditions of technological interest.

Acknowledgement

Work performed under contract with the Commission of the European Communities (EN3E-0168P).

References

1. O. Yamamoto, Y. Takeda, Y. Tomida, M. Noda, *Solid State Ionics*, 22, 241 (1987).
2. V. Narasimhan, H.V. Keer, D.K. Chakrabarty, *Phys. Stat. Sol. (a)*, 89, 65 (1985).
3. Y. Ohno, S. Nagata, H. Sato, *Solid State Ionics*, 9&10, 1001 (1983).
4. A. Hammouche, S. Siebert, A. Hammou, *Mat. Res. Bull.*, 24, 367 (1989).
5. F.M.B. Marques, J.A. Labrincha, J.R. Frade, A.P.M. Carvalho, D.M. Sá, *Euro-Ceramics*, ed. G. de With et al., Vol. 2, p. 246, Elsevier Applied Science, London, (1989).
6. M.J. Verkerk, M.W.J. Hammink, A.J. Burggraaf, *J. Electrochem. Soc.*, 130, [1], 70 (1983).
7. L.G.J. de Haart and de K.J. Vries, *Proc. 1st Int. Symp. on SOFC*, ed. S.C. Singhal, Proc. vol. 89-11, p. 67, The Electrochem. Soc. Inc., (1989).
8. M.A.C.G. van der Graaf, *Science of Ceramics*, ed. K.J. de Vries, Vol. 9, p. 75, The Nederlandse Keramische Vereniging, (1977).
9. H. Ohbayashi, T. Kudo, T. Gejo, *Jap. J. Appl. Phys.*, 13, 1 (1974).
10. E.E. Underwood, *Quantitative Stereology*, Addison-Wesley Publishing Co., London, (1970).
11. T.H. Etsell and S.N. Flengas, *J. Electrochem. Soc.*, 119, [1], 1 (1972).
12. T.H. Etsell and S.N. Flengas, *ibid.*, 118, [12], 1890 (1971).
13. G.P. Wirtz, *Proc. of the DOE Phys. and Chem. Energy Storage Annual Contractors Review Meeting*, Arlington, p. 106 (1983).
14. D.Y. Wang and A.S. Nowick, *J. Electrochem. Soc.*, 126, [7], 1155 (1979).