

NEW ELECTROLYTES FOR Li/SO₂ CELLS

J. SARRADIN*, R. MESSINA and J. PERICHON

*Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, CNRS, U.M. n° 28,
2 rue Henri Dunant, 94320 Thiais (France)*

(Received September 22, 1986; in revised form March 18, 1987)

Summary

Aromatic and aliphatic sulfones and, more particularly, dimethyl sulfone (DMSO₂), used as cosolvents with sulfur dioxide allow the dissolution of various lithium salts. The dependence of the conductivity on the concentration of both lithium salts and DMSO₂ has been studied.

Lithium bromide and LiCl based electrolytes can be obtained with high conductivities, the best being LiBr/DMSO₂/SO₂ ($32 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$) and LiCl/DMSO₂/SO₂ ($21 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$). These conductivities are of the same order of magnitude as those for LiBr/AN/SO₂ electrolytes. However, the high solubility of LiCl in liquid SO₂ — via DMSO₂ — may offer a suitable alternative to the electrolytes currently used in Li/SO₂ cells.

1. Introduction

The choice of high conductivity electrolytes is of great importance in primary and secondary lithium cells. Since large charge and discharge currents can only be obtained with such an electrolyte it would appear that the most promising electrolytes will be based on a solvent with a high dielectric constant and a low viscosity. In addition to conductivity, lithium stability and solvation effects on Li⁺ ions are also of importance. Many mixed aprotic solvent and molten salt electrolytes have been investigated so far. Our work, however, is concentrated on the sulfone-based electrolytes. These form an interesting group of organic solvents due to their physical and chemical properties. In addition, dimethyl sulfone (DMSO₂) and tetramethylene sulfone (sulfolane) have been shown to give rise to a weak solvation effect [1, 2]. The only single-sulfone solvents which have been investigated are sulfolane and its derivative, 3 methylsulfolane [3 - 6]. Sulfolane, used alone or mixed, has already been proposed as an electrolyte for lithium batteries [7, 8].

*Author to whom correspondence should be addressed. Present address: Laboratoire de Physicochimie des Matériaux, U.A. 407 - U.S.T.L. Place Eugène Bataillon - 34060 Montpellier Cédex, France.

Some investigations on DMSO₂ have been carried out in our laboratory [9] for application at 150 °C. The usefulness of DMSO₂ as a co-solvent with SO₂ (or other solvents) for lower temperature application has never been examined. Such mixtures may constitute new electrolytes for Li/SO₂ cells.

Sulphur dioxide alone is a very poor solvent, and an organic co-solvent such as acetonitrile is necessary to promote the solubility of lithium salts. With regard to the high conductivity observed in DMSO₂-based electrolytes, the lithium salts/SO₂/DMSO₂ mixture may have a conductivity suitable for high specific energy lithium batteries. Determination of the conductivity of various lithium salts dissolved in sulfones, and especially in DMSO₂/SO₂ mixtures over the temperature range -35 °C to +10 °C, are presented in this paper.

2. Experimental

Dimethyl sulfone (DMSO₂) sulfolane (S), n-propyl sulfone and 3-methylsulfolane (3-MeS) were obtained from Janssen. Dimethyl sulfone was first dissolved in boiling water, recrystallized twice from methanol, air dried, and finally redried under vacuum at 30 °C for 12 h. Sulfolane was bi-distilled under reduced pressure. n-Propyl sulfone and 3-MeS were used without further purification.

Several lithium salts were investigated: LiBr, LiCl, LiAsF₆, LiClO₄, LiBF₄ and LiCF₃SO₃. LiBr was obtained from SAFT America Inc., and was used as received. The LiCl, from Prolabo, was dehydrated with HCl at 250 °C and then dried under vacuum for 5 h at the same temperature. "Electrochemical Grade" LiAsF₆, from USS Agri-Chemical, was used without further purification. LiClO₄, LiBF₄ and LiCF₃SO₃, from Fluka, were dried under reduced pressure at various temperatures for 12 h. All of these lithium salts were stored and dispensed by weight in an argon-filled dry box.

The sulfur dioxide was supplied by Matheson Co. and contained less than 100 p.p.m. of water. The preparation of the lithium salt/DMSO₂/SO₂ mixture was carried out by bubbling SO₂ through DMSO₂ at -10 °C. Then the lithium salt was added to the liquid mixture, SO₂/DMSO₂. The experimental cell (Fig. 1) was thermostatically controlled to within ±0.2 °C while the electrolytic conductivities were measured with an impedance bridge which was considered to be sufficiently accurate for the present purpose.

3. Results and discussion

(a) Effect of the type of sulfone

As lithium perchlorate is poorly soluble in SO₂ a cosolvent is necessary. We have studied the conductivity of various mixed solvents con-

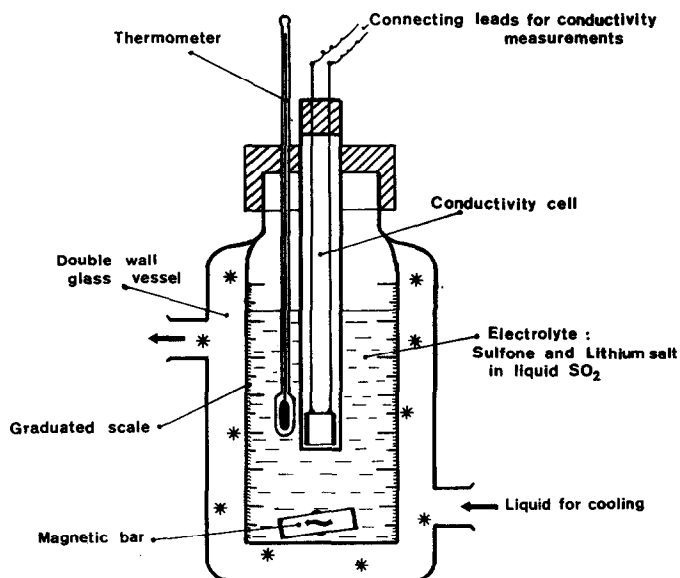


Fig. 1. Experimental cell.

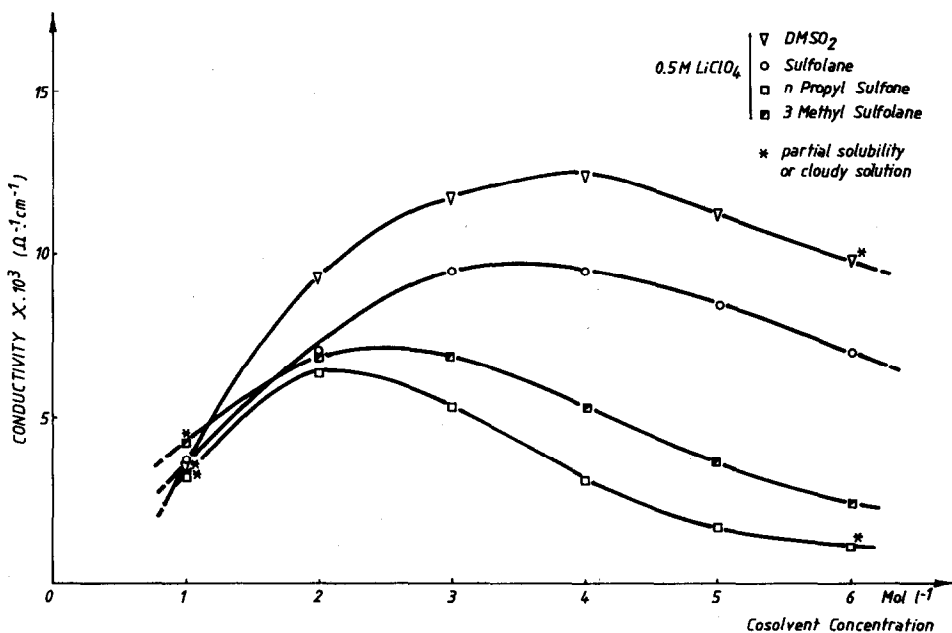


Fig. 2. Conductivity of 0.5 M LiClO_4 in liquid sulfur dioxide at -10°C as a function of sulfone concentration.

taining 0.5 M LiClO_4 since it has been reported that sulfolane, used as a cosolvent, increases an electrolyte's conductivity [7]. Among the sulfone/ SO_2 mixtures studied, the best results were obtained when DMSO_2 was used (Fig. 2).

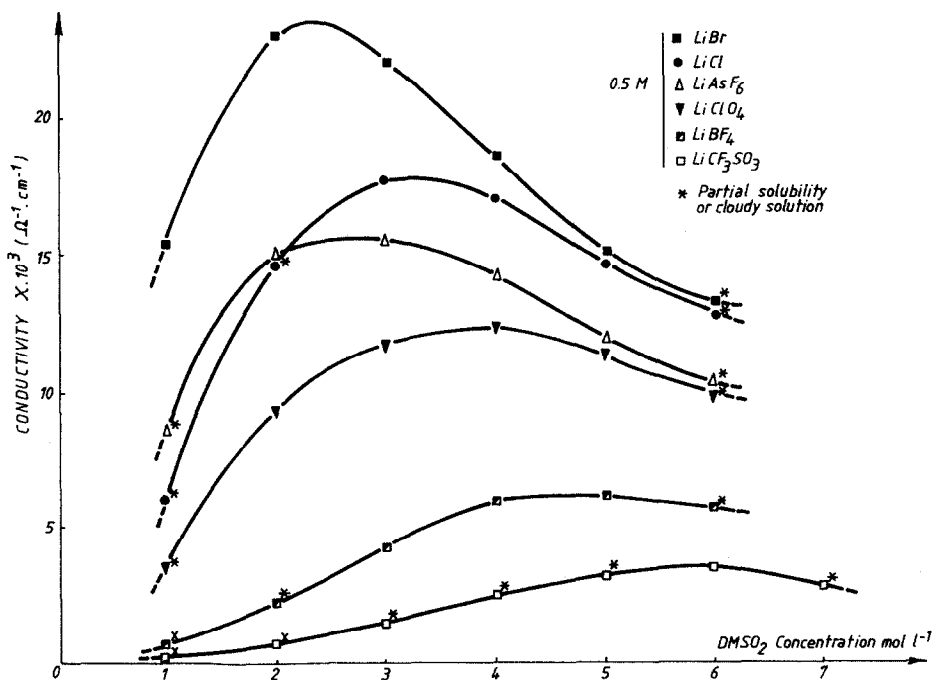


Fig. 3. Conductivity of various 0.5 M lithium salts in liquid sulfur dioxide at -10°C as a function of DMSO_2 concentration.

(b) Effect of different lithium salts

Because of the good conductivity of $\text{LiClO}_4/\text{DMSO}_2/\text{SO}_2$ electrolytes, some other lithium salts were tested. Figure 3 shows the conductivity dependence on DMSO_2 concentration in liquid SO_2 for various lithium salts. From these results, it can be concluded that:

— lithium salts have significantly different conductivities; high in the cases of LiBr , LiCl , LiAsF_6 and even LiClO_4 , while LiBF_4 and LiCF_3SO_3 are not so attractive;

— most of the lithium salts studied are partly soluble: particularly in DMSO_2 concentrations $\leq 1\text{ M}$ or $\geq 6\text{ M}$;

— substantial increases in conductivity were observed for most lithium salts in 3 M or 4 M DMSO_2 concentrations. A co-solvent effect was also noted with DMSO_2 as with the other sulfones studied.

So, $\text{SO}_2/\text{DMSO}_2$ mixtures may allow the use of lithium salts other than LiAlCl_4 [10].

(c) Lithium salt concentration effects

From the above results, a 3 M DMSO_2 concentration appears to be the optimum composition with liquid SO_2 for dissolving increasing amounts of lithium salts. Figure 4 shows the high conductivities obtained with LiBr , LiCl and LiAsF_6 , peaking at a concentration of about 0.75 M in the case

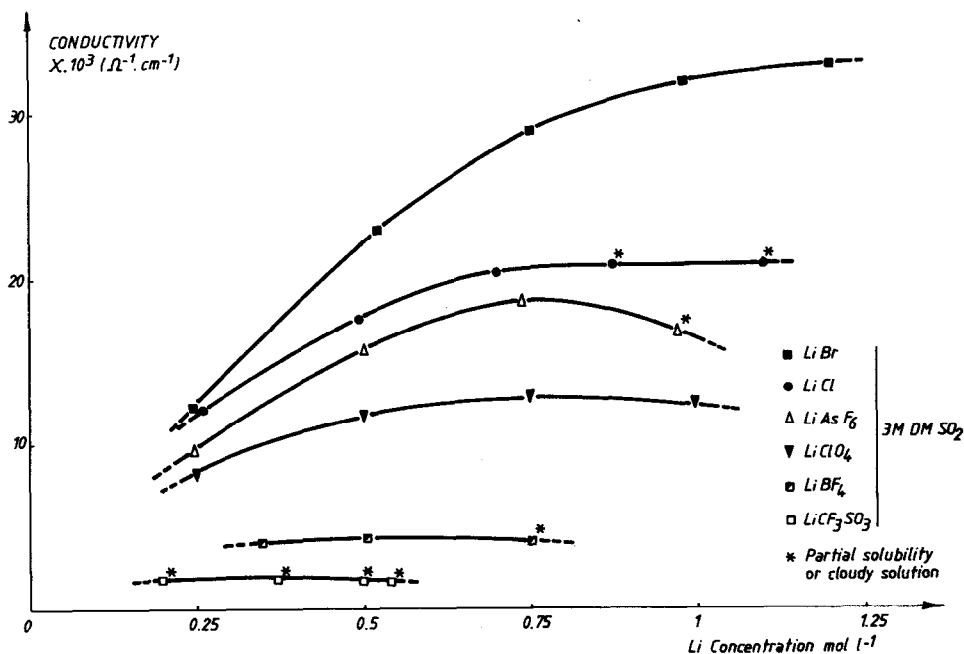


Fig. 4. Conductivity of various lithium salts/3 M DMSO_2 in liquid sulfur dioxide at -10°C as a function of Li concentration.

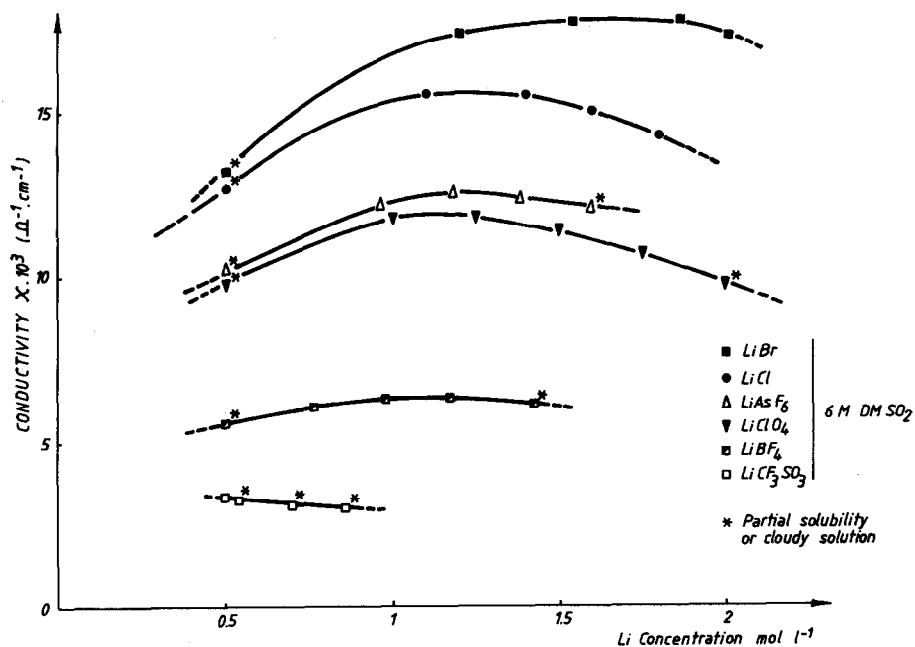


Fig. 5. Conductivity of various lithium salts/6 M DMSO_2 in liquid sulfur dioxide at -10°C as a function of Li concentration.

of LiAsF_6 and at even higher concentrations in the case of LiBr , which is very soluble in this mixture and which gave the highest conductivity of $32 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at a strength of 1.25 M.

(d) DMSO_2 concentration effect

The partial solubility of lithium salts observed in 3 M DMSO_2 may be overcome by increasing the amount of DMSO_2 in the mixture. In 6 M DMSO_2 concentration, all lithium salts except LiCF_3SO_3 are fully dissolved at higher concentrations (≥ 1 M) (Fig. 5).

The conductivity values, however, are lower in 6 M DMSO_2 than in 3 M DMSO_2 . Although increasing the DMSO_2 concentration greatly enhances the solubility of lithium salts there is no obvious correlation between these

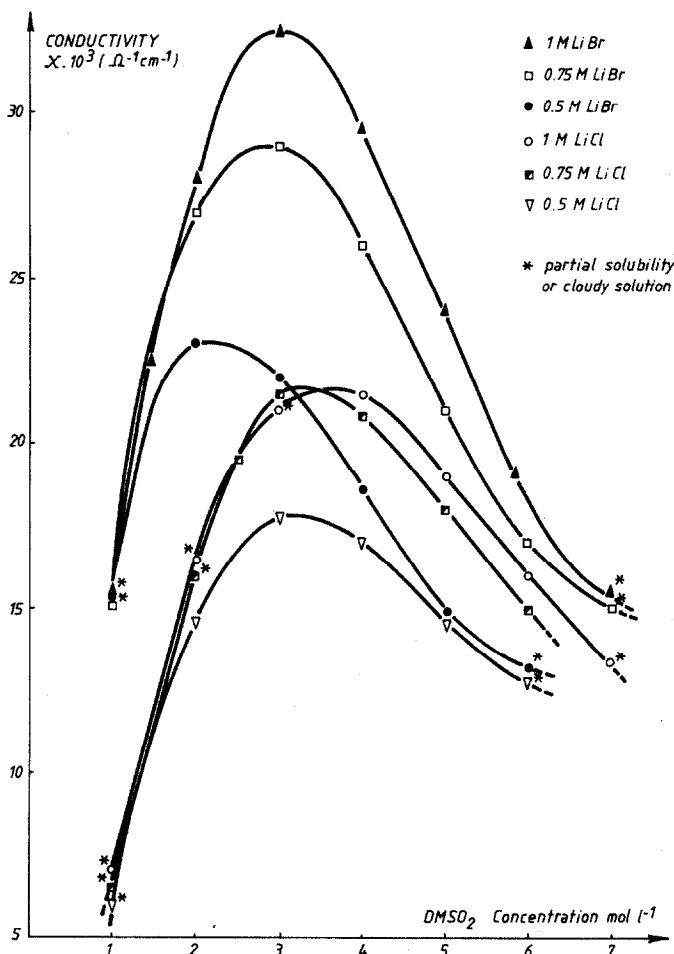


Fig. 6. Conductivity vs. DMSO_2 concentration at -10°C for LiCl and LiBr based electrolytes in liquid sulfur dioxide.

parameters. For example, almost all lithium salts at 0.5 M concentration are entirely dissolved in 3 M DMSO₂ (Fig. 4) but not in 6 M DMSO₂, in contrast to all expectations (Fig. 5). Such a phenomenon suggests a complex effect of ion solvation between DMSO₂ and SO₂ in these ternary mixtures. Increasing DMSO₂ concentration, however, allows the dissolution of large amounts of lithium salts such as LiBr and LiCl (Fig. 6). These electrolytes are very attractive and their conductivities are close to those reported for Li/SO₂ cell electrolytes [11].

(e) Temperature effect

A 1 M LiBr/3 M DMSO₂/SO₂ electrolyte and a 0.75 M LiCl/3 M DMSO₂/SO₂ electrolyte have been investigated at lower temperatures. These electrolytes remain clear to temperatures of -35 °C and the conductivities (Fig. 7) remain attractive. One of the most important advantages concerns the LiCl based electrolyte. It is not used in Li/SO₂ cells because of its low solubility [12], but via DMSO₂, its solubility in liquid SO₂ is greatly enhanced. In addition, LiCl is more stable and less expensive than LiBr and LiCl/DMSO₂/SO₂ may be a promising electrolyte for Li/SO₂ cells. Such an electrolyte has been tested in cells by SAFT America Inc. [13].

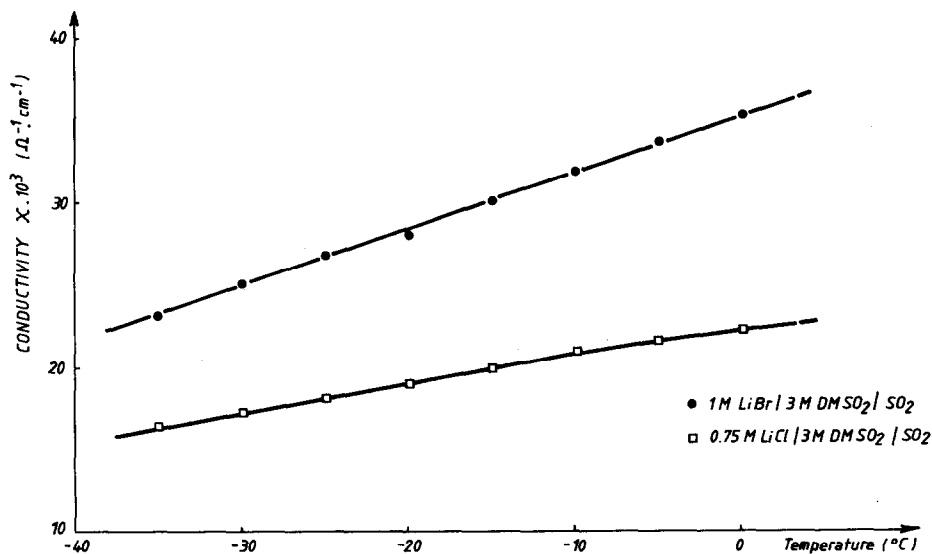


Fig. 7. Conductivity dependence on temperature for 0.75 M LiCl/3 M DMSO₂/SO₂ and 1 M LiBr/3 M DMSO₂/SO₂ electrolytes.

4. Conclusion

The utilization of sulfones and, more especially, DMSO₂ as cosolvents with SO₂ and Li salts such as LiCl or LiBr allows the formation of electrolytes with high conductivities over a large temperature range. Moreover,

these electrolytes do not contain acetonitrile, a co-solvent which may incur safety problems, especially if the Li/SO₂ cells are shortcircuited. LiCl is cheaper and also more chemically stable than LiBr. LiCl with DMSO₂ as cosolvent, therefore, appears to be attractive and, perhaps, could lead to a new generation of Li/SO₂ cells with improved safety and stability.

Acknowledgements

Funding for this work was provided by Direction des Recherches, Etudes et Techniques (D.R.E.T.). The authors thank Dr J. P. Gabano (S.A.F.T., France) for helpful discussions.

References

- 1 B. Bry, *Thèse de Doctorat d'Etat*, Paris, 1976.
- 2 J. F. Coetzee, *Pure Appl. Chem.*, 49 (1977) 217.
- 3 Fernandez-Prini and J. E. Prue, *Trans. Faraday Soc.*, 62 (1966) 1257.
- 4 M. Spiro, in A. K. Covington and T. Dickinson (eds.), *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, 1973.
- 5 L. M. Mukerjee, *Crit. Rev. Anal. Chem.*, 4 (1975) 325.
- 6 B. J. Carter, S. P. S. Yen, D. H. Shen, R. M. Williams and R. B. Somoano, *Ext. Abstr. Fall Meeting, Electrochemical Society, Denver, CO, October, 1981*, The Electrochemical Soc. Inc., NJ, Vol. 81.2.
- 7 J. S. Foos, L. S. Rembetsy and S. F. Brummer, *E.I.C. Laboratories, Inc. Final Rep. Dept. of Energy, Contract No. DE-ACO3-76 SF 00098*, Sept. 1984.
- 8 Y. Matsuda, M. Morita, K. Yamada and K. Hirai, *J. Electrochem. Soc.*, 132 (1985) 2538 - 2542.
- 9 J. P. Pereira-Ramos, R. Messina and J. Perichon, *J. Power Sources*, 16 (1985) 193 - 204.
- 10 Duracell International Inc., *French Pat. No. 83-13038*.
- 11 C. R. Walk, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, 1983, p. 281.
- 12 H. V. Venkatesetty, D. J. Saathoff and P. M. Shah, in B. B. Owens and N. Margalit (eds.), *Proc. Symp. on Ambient Temp. Lithium Batteries*, The Electrochemical Soc. Inc., NJ, 1980, pp. 560 - 569.
- 13 J. P. Gabano, J. Sarradin, R. Messina and J. Perichon, *French Pat. No. 86-10096*, July, 1986.