Proton Conductivity in Nafion® 117 and in a Novel Bis[(perfluoroalkyl)sulfonyl]imide Ionomer Membrane

J. J. Sumner, S. E. Creager,* J. J. Ma, and D. D. DesMarteau

Department of Chemistry, Clemson University, Clemson, South Carolina 29634, USA

ABSTRACT

A study of proton conductivity in a commercial sample of Nafion® 117 and a structurally similar bis[(perfluoroalkyl)sulfonyl]imide ionomer membrane under variable temperature and humidity conditions is reported. The sulfonyl imide ionomer was synthesized using a novel redox-initiated emulsion copolymerization method, and conductivities were measured using a galvanostatic four-point-probe electrochemical impedance spectroscopy technique. Both materials exhibited a strong dependence of conductivity on temperature and humidity, with conductivity in both cases being strongly diminished with decreasing humidity (at constant temperature) and increasing temperature (at constant water partial pressure). The observed behavior is consistent with a "liquid-like" mechanism of proton conductivity whereby protons are transported as hydrated hydronium ions through water-filled pores and channels in the ionomer.

Introduction

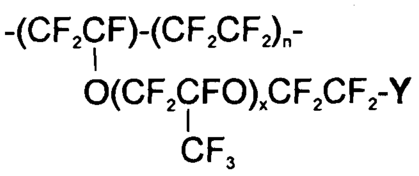
Fuel cells based on proton exchange membranes (PEMs) have been identified as promising power sources for vehicular transportation and other applications requiring clean, quiet, and portable power.[1,2] Fuel-cell-based power sources in general have a high power density and are relatively efficient (compared to internal combustion engines) in their conversion of chemical to electrical energy. Exhaust from fuel-cell-based power sources is free of environmentally undesirable gases such as nitrogen oxides, carbon monoxide, and residual hydrocarbons that are commonly produced by internal combustion engines. Carbon dioxide, a greenhouse gas, is also absent from the exhaust of fuel-cell-based power sources when hydrogen is used as fuel.[3]

A limiting factor in PEM fuel-cell technology is the membrane that serves as a structural framework to support the electrodes and transport protons from the anode to the cathode. The membrane material that has been used in most PEM fuel-cell research and development work to date is a sulfonic-acid-based perfluorinated ionomer produced by DuPont under the trade name Nafion®. Nafion has many desirable properties including good mechanical strength, good chemical stability, and high ionic conductivity, particularly under high-humidity conditions.[4,5] Limitations include poor ionic conductivity at low humidity and/or elevated temperatures[6-9] and a susceptibility to chemical degradation at elevated temperatures.[10] These factors can adversely affect fuel-cell performance and limit the conditions under which a fuel cell may be operated.

Recent work by DesMarteau and co-workers[11] aimed at developing synthetic routes to a new class of ionically conductive polymers based on the bis[(perfluoroalkyl)sulfonyl]imide moiety may provide an alternative to sulfonic acid-based ionomers for PEM fuel cell membranes. Sulfonyl imides are among the strongest gas-phase superacids known,[12] and they have been shown to possess excellent thermal stability. Preliminary work has suggested that sulfonyl imide ionomers possess properties which may be useful in fuel-cell applications, particularly regarding their thermal stability and their capacity to promote facile fuel-cell reactions (oxygen reduction and fuel oxidation) at catalyst/ionomer interfaces.[13-15] The sulfonyl imide moiety also possesses two independent sites for structural modification, as compared with the single site available in sulfonic acids. Thus, there may be greater opportunity for optimizing ionomer properties with sulfonyl imides through chemical variation of the ionomer primary structure.

This report describes the results of a study of proton conductivity in Nafion 117 and a structurally similar sulfonyl imide ionomer. The structures of the two ionomers are shown in Scheme 1. The sulfonyl imide ionomer is chosen to have an equivalent weight close to the value of 1100 quoted by the manufacturer for a Nafion 117 membrane, so differences in conductivity associated with differences in acid site loading for the two materials should be minimal. Conductivities were measured over a broad range of water activities (humidities) and temperatures, since these are the critical operational parameters in hydrogen-oxygen PEM fuel-cell technology. Also, prior work with Nafion has indicated that temperature and humidity play important roles in dictating ionic conductivity.[6-9] Conductivity was measured using a galvanostatic four-point-probe electrochemical impedance spectroscopy technique to minimize contributions to the impedance from contact resistance at the current-carrying electrodes.[7,16]

Scheme I



$$\begin{array}{l} -(CF_2CF)-(CF_2CF_2)_n- \\ \qquad\quad | \\ \qquad\quad O(CF_2CFO)_xCF_2CF_2\text{-}Y \\ \qquad\qquad\qquad | \\ \qquad\qquad\qquad CF_3 \end{array}$$

Nafion 1100 E.W.; $Y = \text{-}SO_3H$, $n = 6.6$

Sulfonyl imide; $Y = \text{-}SO_2NHSO_2CF_3$, $n = 5.1$

Conductivity in both Nafion and the sulfonyl imide ionomer was found in this work to depend strongly on humidity and temperature. This dependence can be understood in terms of a "liquid-like" mechanism of proton conductivity whereby protons are transported as hydrated hydronium ions through water-filled ionic pores and channels.[17]

Experimental

Ionomer synthesis and membrane fabrication.—Functionalized monomers used to prepare the bis[(perfluoroalkyl)sulfonyl]imide ionomers were synthesized as described in ref. 11 Ionomers were prepared by copolymerization of functionalized monomers with tetrafluoroethylene by a redox-initiated aqueous emulsion copolymerization that is also described in Ref. 11. Ionomer membranes were fabricated by casting the soluble ionomers from dimethylformamide solution followed by solvent removal under vacuum at 60°C. Membranes were treated with 70% HNO_3 followed by 15% HCl and were then annealed in vacuum at 200°C.

Prior to their use in conductivity experiments, membranes were subjected to a pretreatment regime including soaking in 70% HNO_3 followed by boiling sequentially in 3% H_2O_2, 5% HCl, and deionized water, each for 1 h. The H_2O_2 served to oxidize any small-molecule contaminants that might block the ion-conduction channels, the HCl reverted all acidic sites to the proton form, and the deion-

---

* Electrochemical Society Active Member.

ized water rinsed away the excess acid. This pretreatment cleared up the discoloration that was typically present in the membranes as received and should leave the ionomers in the "E-form" according to the classification scheme of Yeo and Yeager.[5] Membranes were stored under deionized water after pretreatment but prior to use in conductivity experiments.

Conductance and water uptake measurements.—A four-point-probe conductivity cell with two palladium foil outer current-carrying electrodes and two platinum wire inner potential-sensing electrodes was fabricated from Teflon. The cell geometry is illustrated in Fig. 1. Membrane samples were cut into strips that were approximately 0.33 cm wide, 2 cm long, and 0.02 cm thick prior to mounting in the cell. More precise measurements were made on individual samples immediately prior to mounting. Conductance measurements were made using a Solartron SI 1280B electrochemical impedance analyzer with ZPLOT for Windows software (Version 1.2). The instrument was used in galvanostatic mode with an ac current amplitude of 0.01 mA over a frequency range from 0.1 to 20,000 Hz. Water uptake was determined gravimetrically for membranes that were first dried by exposure to a P_4O_{10} dessicating environment for 4 h, followed by exposure to the specified relative humidity environment for 4 h.

Environmental control.—Humidity control at room temperature was achieved using concentrated salt solutions in a sealed container similar to that described in Ref. 8. Saturated $CaCl_2$ was used to produce a 31% relative humidity environment and saturated $(NH_4)_2SO_4$ was used to produce a 81% relative humidity environment.[18,19] Literature values for the humidity in the headspace above the salt solutions were verified using a Fisher Model 11-661-7A hygrometer. To obtain a 100% relative humidity environment, deionized water was used, and for a 0% relative humidity environment, solid P_4O_{10} was placed in the bottom of the chamber.

Experiments at elevated temperature (60 to 105°C) and fixed water partial pressure were performed using the apparatus illustrated in Fig. 2. Dry nitrogen was passed through a water-filled bubbler at 60°C to saturate the nitrogen with water vapor at 2.0×10^4 Pa (150 Torr).[18] Copper tubing was used to transfer the wet nitrogen from the bubbler to a glass chamber inside a Baxter Scientific Products Model N7595-1 vacuum oven from which the vacuum ports had been removed to enable electrical connections and gas-transfer lines to be routed into the oven. Transfer lines were heated with a heating tape outside the oven to prevent condensation. The transfer line was coiled several times inside the oven to ensure that the temperature of the humidified gas was equilibrated with the oven temperature prior to the gas reaching the conductivity cell.

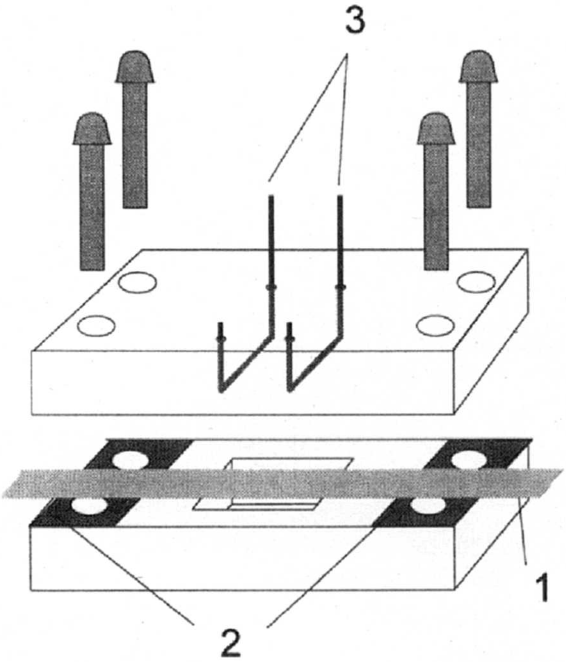


Fig. 1. Four-point-probe conductivity cell for measuring ionic conductivities in ionomer membranes: (1) ionomer, (2) palladium outer electrodes, and (3) platinum inner electrodes. Cell dimensions are approximately 2.5 × 2.5 × 0.5 cm.

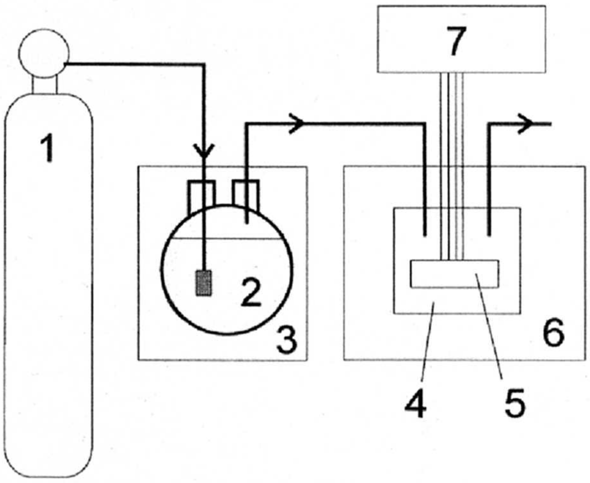


Fig. 2. Controlled-environment apparatus for measuring ionic conductivities at elevated temperatures and humidities: (1) compressed nitrogen, (2) water bubbler, (3) hot-water bath, (4) glass enclosure for conductivity cell, (5) conductivity cell, (6) oven, and (7) electrochemical impedance analyzer.

Results and Discussion

In the galvanostatic four-point-probe method, a fixed ac current is passed between two outer electrodes, and the conductance of the material of interest is calculated from the ac potential difference observed between two inner electrodes. The method is relatively insensitive to the contact impedance at the current-carrying electrodes and is therefore well suited to measuring ionic conductance.[7,16] Bode plots of impedance and phase angle of the potential difference detected at the inner electrodes relative to the current applied at the outer electrodes over a frequency range from 0.1 to 20,000 Hz show that the impedance is approximately invariant with frequency and the phase angle is quite close to zero over the full frequency range, as expected if the material between the inner electrodes is behaving as a nearly ideal pure resistor. Nonzero phase angles were sometimes seen at the higher frequencies, which suggests that capacitive and/or inductive elements can contribute to the measured impedance at these frequencies. Indeed, one advantage of ac methods is that they provide information over a wide frequency range, which makes it relative easy to focus on those regions where the impedance is dominated by the ionic conductance, the property of primary interest in this work. All the conductivity data reported in this paper were obtained using impedance values for which the phase angle is close to zero, so that the impedance is dominated by the ionic conductance.

Figure 3 and Table I present room temperature conductivity data for Nafion 117 and a sulfonyl imide-based ionomer at several representative relative humidities. Both ionomers exhibit a strong decrease in conductivity as humidity decreases, with the decrease being greatest as humidity approaches 0%. The data for Nafion 117 are in

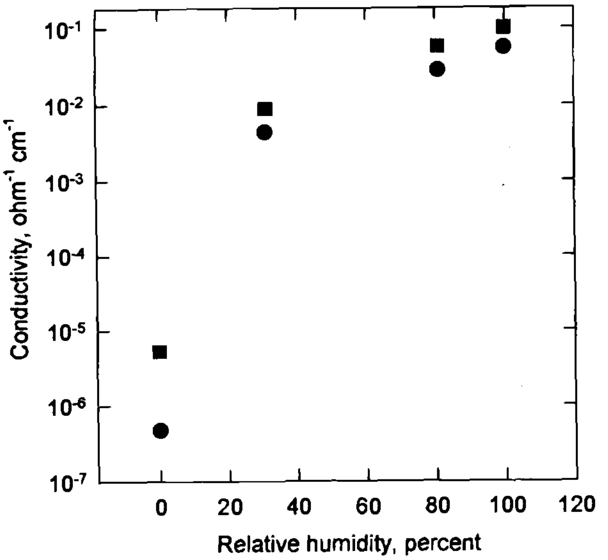


Fig. 3. Log (conductivity) vs. relative humidity plots for Nafion 117 (circles) and sulfonyl imide (squares) obtained at ambient temperature using the galvanostatic four-point-probe method.

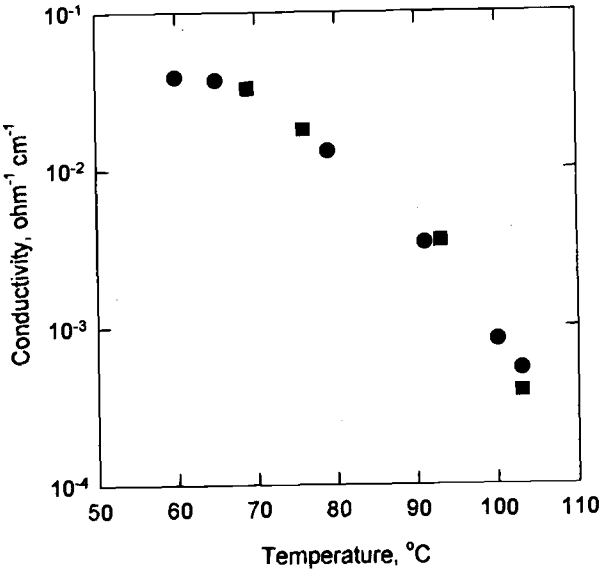


Fig. 4. Log (conductivity) vs. temperature plot for Nafion 117 (circles) and sulfonyl imide (squares) ionomer membranes obtained at a fixed water partial pressure of 2.0 × 10^4 Pa (150 Torr).

good quantitative agreement with values reported by others.[6-9] This strong dependence of conductivity on humidity reflects in part a strong tendency of both sulfonic acid and sulfonyl imide ionomers to absorb water vapor. Table II presents data which illustrate water absorption for both types of ionomer at several different relative humidities. Water absorption is substantial in both ionomers even at a relative humidity of only 31% and increases further as humidity increases. The data for Nafion 117 are again in good quantitative agreement with values reported by others.[20,21]

Figure 4 and Table III present a different comparison of conductivity in sulfonic acid and sulfonyl imide ionomers, this time focusing on the variation of conductivity with temperature at fixed water partial pressure. The particular water partial pressure chosen (2.0 × 10^4 Pa or 150 Torr) corresponds to 100% relative humidity at 60°C and is in the range of values expected for the humidified feed in a practical PEM fuel cell device.[15,22] Both ionomers exhibit a marked decrease in conductivity with increasing temperature, such that conductivity at 105°C has diminished by more than 50 times relative to that at 60°C.

Behavior such as that in Fig. 3 and 4 has been attributed to a "liquid-like" proton conductivity mechanism whereby protons are transported as free hydronium ions through water-filled ionic pores and channels in the ionomer.[17] Membranes became less conductive under low-humidity and/or high-temperature conditions because they dry out, causing the channels to collapse and proton transport to become more difficult. Eventually, as humidity continues to decrease, water is no longer available to hydrate protons, and conductivity is further diminished as acid dissociation becomes more difficult. The fact that both sulfonic acid and sulfonyl ionomers exhibit a similar dependence of conductivity on humidity and temperature strongly suggests that the mechanism of conductivity is generally the same for both materials. Room temperature conductivities were quite similar in both materials at high humidity, suggesting that under such conditions, ionomer structure may play only a relatively minor role in controlling ionic conductivity. In contrast, under very low humidity conditions, the sulfonyl imide exhibited a slightly higher conductivity than Nafion 117. This suggests that the sulfonyl imide ionomer may possess an internal pore and/or channel structure that is more favorable for proton conduction under conditions of low water availability. Alternatively, the acid strength of the anionic groups in the two ionomers may simply be sufficiently different that proton dissociation and mobility are affected. Ongoing studies aimed at further developing methods for the synthesis and processing of these new ionomer materials and at characterizing their structure and acidity under con-

Table I. Room temperature conductivity of Nafion 117 and a sulfonyl imide ionomer.

Relative Humidity	Conductivity (Ω^{-1} cm^{-1}) Nafion 117	Sulfonyl imide
100%	5.5 × 10^{-2}	1.0 × 10^{-1}
81%	2.8 × 10^{-2}	5.7 × 10^{-2}
31%	4.4 × 10^{-3}	8.9 × 10^{-3}
0%[a]	4.7 × 10^{-7}	5.7 × 10^{-6}

[a] Conductivities at 0% relative humidity are best considered as upper limits, as the membranes can take a very long time to become completely dried.

Table II. Water uptake by Nafion 117 and a sulfonyl imide ionomer.[a]

Relative humidity	Weight percent water uptake: Nafion	Sulfonyl imide	Number of waters per acid site: Nafion	Sulfonyl imide
0%	0	0	0	0
31%	6.6%	6.6%	4	4
81%	15%	35%	9	21
100%	31%	116%	19	70

[a] Measured gravimetrically at room temperature, assuming zero water content after 4 h drying of membranes over P_4O_{10}.

Table III. Variable-temperature conductivity of Nafion 117 and a sulfonyl imide ionomer at a fixed water partial pressure of 2.0 × 10^4 Pa (150 Torr).

Temperature (°C)	Conductivity (Ω^{-1} cm^{-1}) Nafion 117	Sulfonyl imide
60	3.9 × 10^{-2}	—
65	3.7 × 10^{-2}	—
69	—	3.3 × 10^{-2}
76	—	1.8 × 10^{-2}
79	1.3 × 10^{-2}	—
91	3.4 × 10^{-3}	—
93	—	3.5 × 10^{-3}
100	8.3 × 10^{-4}	—
103	5.4 × 10^{-4}	3.9 × 10^{-4}

trolled temperature and humidity conditions provide further insight into their intriguing properties.

Acknowledgments

Financial support of this work by the U.S. Department of Energy EPSCoR program is gratefully acknowledged.

Manuscript submitted April 23, 1997; revised manuscript received July 22, 1997.

Clemson University assisted in meeting the publication costs of this article.

REFERENCES

1. A. J. Appleby and F. R. Foulkes, *Fuel Cell Handbook*, Van Nostrand Reinhold, New York (1989).
2. G. Pourcelly and C. Gavach, in *Proton Conductors, Solids, Membranes, and Gels-Materials and Devices*, P. Colomban, Editor, Cambridge University Press, Cambridge (1992).
3. V. Plzak and B. Rohland, in *Modern Aspects of Electrochemistry*, No. 26, B. E. Conway, Editor, p. 105. Plenum Press, New York (1994).
4. G. Pourcelly and C. Gavach, in *Proton Conductors, Solids, Membranes, and Gels- Materials and Devices*, P. Colomban, Editor, Cambridge University Press, Cambridge (1992).
5. R. S. Yeo and H. L. Yeager, in *Modern Aspects of Electrochemistry*, No. 16, B. E. Conway, R. E. White, and J. O'M. Bockris, Editors, pp. 437-504, Plenum Press, New York (1985).
6. T. A. Zawodzinski, T. E. Springer, F. Uribe, and S. Gottesfeld, *Solid State Ionics*, **60**, 199 (1993).
7. Y. Stone, P. Ekdunge, and K. Simonsson, *This Journal*, **143**, 1254 (1996).
8. F. Opekar and D. Svozil, *J. Electroanal. Chem.*, **385**, 269 (1995).
9. M. Cappadonia, U. Linke, K. M. Robinson, J. Schmidberger, and U. Stimming, *ibid.*, **405**, 227 (1996).
10. S. R. Samms, S. Wasmus, and R. F. Savinell, *This Journal*, **143**, 1498 (1996).
11. D. D. DesMarteau, *J. Fluorine Chem.*, **72**, 203 (1995).
12. I. A. Koppel, R. W. Taft, F. Anvia, S.-Z. Zhu, L.-Q. Hu, K.-S. Sung, D. D. DesMarteau, L. M. Yagupolskii, Y. L. Yagupolski, N. V. Ignat'ev, N. V. Kondratenko, A. Y. Volkonskii, V. M. Slasov, R. Notario, and P.-C. Maria, *J. Am. Chem. Soc.*, **116**, 3047 (1994).
13. M. Razaq, A. Razaq, E. Yeager, D. D. DesMarteau, and S. Singh, *J. Appl. Electrochem.*, **17**, 1057 (1987).
14. M. Razaq, A. Razaq, E. Yeager, D. D. DesMarteau, and S. Singh, *This Journal*, **136**, 385 (1989).
15. A. J. Appleby, O. A. Velev, J.-G. LeHelloco, A. Parthasarthy, S. Srinivasan, D. D. DesMarteau, M. S. Gillette, and J. K. Ghosh, *ibid.*, **140**, 109 (1993).
16. B. D. Cahan and J. S. Wainright, *ibid.*, **140**, L185 (1993).
17. K. D. Kreuer, *Chem. Mater.*, **8**, 610 (1996).
18. *CRC Handbook of Chemistry and Physics*, D. R. Lide, Editor, CRC Press, Boca Raton, FL (1990).
19. L. Greenspan, *J. Res. Natl. Inst. Stand.*, **81A**, 89 (1976).
20. J. T. Hinatsu, M. Mizuhata, and H. Takenaka, *This Journal*, **141**, 1493 (1994).
21. T. A. Zawodzinski, T. E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, and S. Gottesfeld, *ibid.*, **140**, 1981 (1993).
22. P. N. Ross, *ibid.*, **130**, 882 (1983).

Investigations on the Electroreduction of Titanium Chlorides in $AlCl_3$-Dimethylsulfone Electrolyte

L. Legrand, A. Chaussé, and R. Messina

Laboratoire des Matériaux Polymères aux Interfaces, EP 109, CNRS, 94320 Thiais, France

ABSTRACT

The electrochemical behavior of $TiCl_3$ and $TiCl_4$ was studied in $AlCl_3/DMSO_2$ electrolyte at 130°C. The main Ti^{III} and Ti^{IV} species formed in the $AlCl_3/DMSO_2$-based electrolyte might be $TiCl^{n+}_{(3-n)}$ and $TiCl^{m+}_{(4-m)}$, respectively. The reduction of Ti^{IV} to Ti^{II} is a multistep process (one electron transferred in each step). The diffusion coefficient values of Ti^{III} and Ti^{IV} species have been calculated from voltamperometric and chronoamperometric investigations. Analysis of sampled current voltammograms indicates that the Ti^{IV}/Ti^{III} process is a quasi-reversible redox system with $E_{1/2}$ close to 3.575 V vs Li^+/Li and that the reduction of Ti^{III} to Ti^{II} might involve an electrochemical-chemical mechanism, i.e., electron transfer followed by a destructive reaction or a disproportionation of Ti^{II} species. In the 2 to 4 V potential range, metallic titanium deposition is not observed.

Introduction

Interest in light metals such as aluminum and titanium has steadily increased during recent decades as their physical and chemical properties permit the solution of many engineering problems especially in the aircraft, aerospace and vehicle fields.[1] For some applications in corrosion and optics, the use of metal or alloy deposits are preferred. Among the procedures that can be carried out for the deposition of a metal, electrodeposition is a good tool because it generally offers the possibility to control the thickness of the deposit and even its composition and microstructure in some cases. Many workers have focused their attention on electrolytes in which aluminum electrodeposition operates at moderate temperatures.[2-4] The main types of prospective electrolytes developed for aluminum electrodeposition are the following baths: organoaluminum electrolytes,[5,6] etherhydride[7-9] $AlBr_3$-alkylbenzene electrolytes with HBr[10,11] or MBr[12,13] added, and inorganic[14,15] and organic[16-19] chloroaluminate melts. The possibility of extracting titanium from $TiCl_4$ electrochemically in fused salts was demonstrated by Huppertz 90 years ago.[20] This electroplating process has been extensively studied in alkali chloride and fluoride melts (see Ref. 21 and references therein).

Recently, Stafford et al., reported the electroplating of Al/Ti alloys from acidic mixtures of $AlCl_3$ and NaCl in which titanium had been anodically dissolved.[22,23] Aluminum-titanium intermetallic compounds are ordered alloys which exhibit excellent high-temperature properties for structural and corrosion protective applications.

In previous papers,[24] we reported the development of new electrolytes based on mixtures of $AlCl_3$ and dimethylsulfone ($DMSO_2$). These electrolytes are very simple in terms of preparation, exhibit conductivities which are rather high (16 mS cm^{-1} at 130°C for a molality of 1 mol kg^{-1}), and operate over a temperature interval of 80 to 150°C which allowed us to electroplate aluminum. By ^{27}Al NMR[25] and Raman[26] analysis of $AlCl_3/DMSO_2$ mixtures, we identified two main soluble aluminum species, $AlCl_4^-$ and $Al(DMSO_2)_3^{3+}$, formed from the following solvolysis reaction

$$4AlCl_3 + 3DMSO_2 \rightarrow Al(DMSO_2)_3^{3+} + 3AlCl_4^- \quad [1]$$