

Electrochemical Behaviour of Nafion[†] Gels loaded with Ferrocene and Copper(I) Diphenylphenanthroline Complexes

P. Audebert,^a B. Divisia-Blohorn,^b J. M. Kern,^c and P. Aldebert^d

^a Laboratoire d'Electrochimie Moléculaire, Université de Paris VII, 2 Place Jussieu, 75005 Paris, France

^b Equipe d'Electrochimie Moléculaire, DRF/LCH/EM, Centre d'Etudes Nucléaires de Grenoble, 85 X, F-38041 Grenoble Cedex, France

^c Institut de Chimie, Université Louis Pasteur, 1 Rue Blaise Pascal, F-67008 Strasbourg Cedex, France

^d Groupe de Physico-Chimie Moléculaire, DRF/SPH, Centre d'Etudes Nucléaires de Grenoble, 85 X, F-38041 Grenoble Cedex, France

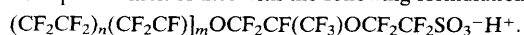
Nafion gels made with hydrophobic solvents can be loaded with electroactive compounds such as ferrocene and behave as electrode coatings which exhibit the mechanical properties of a solid polymer and the electrochemical properties of an electrolytic solution.

Perfluorinated ionomers, like Nafion,[†] are attracting increasing interest because of their wide range of applications, especially in the field of electrochemistry, *e.g.* in electrolyzers or fuel cells.¹ Recently, it has been shown that concentrated solutions (30–50%) of Nafion in various sufficiently polar solvents can lead to gels² which are, in fact, a complex mixture of liquid and solid phases.³ These compounds have ionic conductivities in the range of solution values⁴ while their mechanical properties resemble those of solids.

Nafion gels hold promise in such fields as accumulators or electrochemical catalysis; however, they are still almost completely ignored in this respect in comparison with the abundant literature on modified electrodes⁵ with Nafion films containing electroactive species.⁶ This arises because of the relatively recent discovery of Nafion high equivalent weight solutions and gels,^{7–9} and also the difficulties encountered in developing an electrochemical device, adapted to studies of these, which does not waste the expensive ionomers.

The gels were prepared from Nafion powder crushed at low temperature and solvents such as dibutylformamide (DBF) or tributyl phosphate (TBP). Such gels possess good ionic conductivity, a large electro-inactivity potential range and, moreover, are totally immiscible with water so that the cell described in Figure 1 could be easily constructed, the water

[†] Nafion is a registered trade mark of Dupont de Nemours Co. for its perfluorosulphonic membranes with the following formulation:



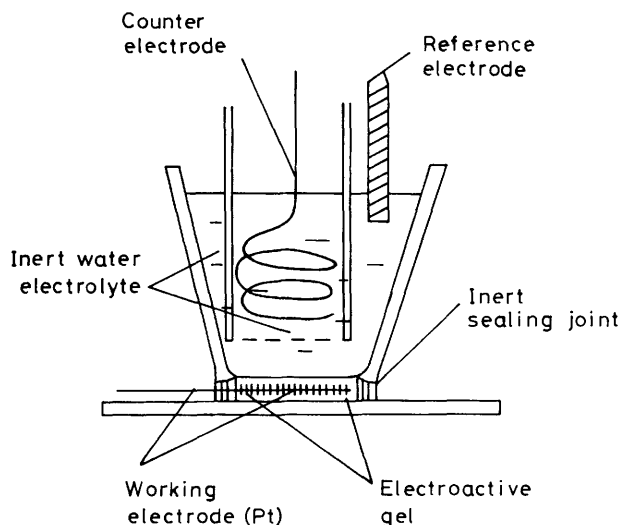


Figure 1. The electrochemical cell. The platinum grid electrode is fully immersed in the gel (surface area of the grid 0.24 cm²).

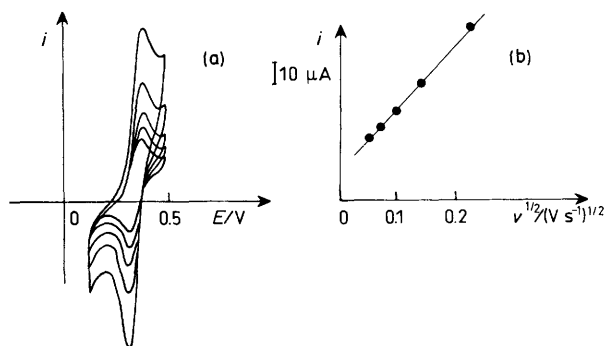


Figure 2. (a) Cyclic voltammetry of bis(2,9-diphenyl-1,10-phenanthroline)copper(I) in a Nafion gel loaded with 10% of carbon powder at different scan rates from 2 (lower curve) to 50 (upper curve) mV s⁻¹. (b) Plot of currents vs. the square root of sweep rates for the same system (solvent of the gel: TBP).

electro-inactive electrolyte ensuring the electrochemical junction. A platinum grid of area 0.24 cm² immersed in the gel was chosen as the working electrode to avoid border effects observed with flat electrodes.

In a typical experiment, 2–3 mg of electroactive compound, 150 mg of Nafion powder, H⁺ exchanged,[‡] prepared as reported,^{2–4} and 175 mg of DBF or TBP, were poured into a beaker. Acetonitrile (0.5 ml) was then added to fluidize the mixture, which is transferred to the bottom of the cell and allowed to dry overnight to remove completely the acetonitrile. The cell was then weighed and an electrolyte composed of doubly distilled water (Millipore) and tetraethylammonium trifluoromethanesulphonate (TEATF) was added for the

[‡] Although we are aware that Li⁺ or Na⁺ exchanged Nafion could be more appropriate than H⁺, because of possible perturbations due to the polymer acidity, we found that cracking effects arise when Li⁺ or Na⁺ exchanged Nafion TBP or DBF gels come in contact with water, which prevented us from obtaining sufficiently stable systems for successful experiments.

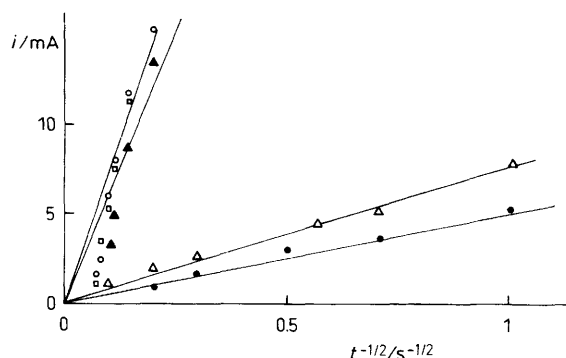


Figure 3. Chronoamperometric plots of a ferrocene containing Nafion gel loaded with 0% (●), 5% (△), 10% (▲), 20% (○), and 30% (□) of carbon powder (solvent of the gel: TBP).

Table 1. Efficiency of the conversion of the electroactive material as a function of the relative carbon powder vs. dry Nafion content of the gel (electroactive compound: ferrocene; gel solvent: TBP; values for the first cycle).

% Carbon powder loading	0	5	10	20	30
% Conversion ^a	7	14	80	63	66
c/g l ⁻¹ b	30	30	29	32	29

^a Conversion of electroactive compound in the first electrochemical cycle. ^b Concentration of electroactive compound.

electrochemical studies. The electrolyte salt was chosen in order to minimize the interfacial difference of potential between the organic gel and the aqueous electrolyte above. The redox potential, E_1 , measured *via* this cell after cyclic voltammetry is 0.29 V (vs. standard calomel electrode, S.C.E.) for ferrocene while the reported value in an organic medium is 0.307 V,¹⁰ which validates this working hypothesis.

The two electroactive compounds studied were ferrocene (Fc) and bis(2,9-diphenyl-1,10-phenanthroline)copper(I).¹¹ In addition, we tested the effect of adding from 0 to 30% of carbon powder to the gel, relative to the dry ionomer content, to provoke electron percolation and increase the electrode area.

The most recent results on Nafion gels indicate a structure involving a lattice of ~60 Å diameter rods, surrounded by the gel solvent, with the perfluoroalkyl chains inside the rods and the sulphonic groups outside, solvated by the nearest solvent species.³ The electroactive species included dissolve in the gel, and hence probably are in the 'liquid' part of it.

It is thus of importance to examine the electrochemical response of such gels, focusing more especially on the kinetic analysis. Cyclic voltammograms have peak currents varying with the square root of the sweep rate (Figure 2) showing, as expected, a diffusion-controlled process. Chronoamperometric studies confirm this assumption (Figure 3), leading to a value of 10⁻⁶ cm² s⁻¹ for the diffusion coefficient, D , in the case of ferrocene. This high value, lower by only one order of magnitude than values generally measured in solution, confirms the freedom of movement of the ferrocene species in the liquid part of the gel. Therefore, such a system presents the advantage of behaving microscopically as a liquid, but macroscopically as a solid, acting like a modified electrode

with a high charge transfer rate; other polymer coated electrodes have diffusion coefficients in the 10^{-10} region¹² owing to the tightness of bonding between the electroactive species and the polymer matrix.

We have also shown that the efficiency of the electrode could be significantly enhanced by adding carbon powder to the gel; comparison between the Cottrell slopes in Figure 3 shows the occurrence of higher currents followed by a faster decrease, which are a consequence of the equivalent of an average ten times increase in the electrode area. Since this increase arises from a 5–10% loading of carbon powder in the gel, the percolation limit between the carbon grains in the loaded gel must be between these values. Such carbon loadings allow the conversion of the main part of the electroactive compound inside the gel, as shown by the results in Table 1, with conversion yields of ferrocene between 60 and 80% for carbon loadings above 10% in the gel. These high conversion yields are related to a fast consumption of the electroactive materials included in the gel, which in addition accounts for the slight deviation observed in the Cottrell plots at long times in these cases.

Electroactive hydrophobic Nafion gels thus combine the electrochemical properties of a liquid electrolyte and the mechanical properties of a solid polymeric electrode modifier, which make them extremely attractive materials for electrochemical catalysis or ion capturing. In addition, the gels can be loaded with carbon, making the whole system behave like a high-performance, mechanically or electrochemically modified, carbon paste electrode.

We thank Dr. C. P. Andrieux and Dr. P. Hapiot for their kind and helpful advice.

Received, 23rd January 1989; Com. 9/00373H

References

- 1 S. Srinivasan, E. A. Ticianelli, C. R. Derouin, and A. Redondo, *J. Power Sources*, 1988, **22**, 359; H. Takenaka, E. Torikai, Y. Kawami, and N. Wakabayashi, *Int. J. Hydrogen Energy*, 1982, **7**, 397; R. Oberlin and M. Fisher, Proceedings of the 6th Hydrogen Energy Conference, Vienna, vol. 1, 1986, p. 333.
- 2 P. Aldebert and M. Pineri, Fr. Pat. 86 05 792 (1986).
- 3 P. Aldebert, B. Dreyfus, G. Gebel, N. Nakamura, M. Pineri, and F. Volino, *J. Phys. France*, 1988, **49**, 2101.
- 4 M. Guglielmi, P. Aldebert, and M. Pineri, *J. Appl. Electrochem.*, 1989, **19**, 167.
- 5 D. W. Dewulf and A. J. Bard, *J. Electrochem. Soc.*, 1988, **135**, 1977.
- 6 Z. Lu and S. Dong, *J. Electroanal. Chem.*, 1987, **233**, 19.
- 7 W. G. Grot and F. Chadds, Eur. Pat. 0066369 (1982).
- 8 C. R. Martin, T. A. Rhoades, and J. A. Ferguson, *Anal. Chem.*, 1982, **54**, 1639.
- 9 P. Aldebert, P. Audebert, M. Armand, G. Bidan, and M. Pineri, *J. Chem. Soc., Chem. Commun.*, 1986, 1636.
- 10 This value was reported for ferrocene in MeCN ('Handbook of Analytical Chemistry,' ed. L. Meites, McGraw-Hill, 1963, pp. 5–154), and is known to be almost constant in a wide variety of organic media.
- 11 C. O. Dietrich-Buchecker, P. A. Marnot, and J. P. Sauvage, *Tetrahedron Lett.*, 1982, **23**, 5291.
- 12 J. Leddy and A. J. Bard, *J. Electroanal. Chem.*, 1985, **189**, 203.