phys. stat. sol. (c) **0**, No. 8, 2944–2948 (2003) / **DOI** 10.1002/pssc.200303847

Drastic improvement of electrical properties of Nafion® 112 membrane on impregnation of bimetallic Au/Pd nanoclusters

U. Pal[*, 1, 3], **J. F. Sánchez-Ramírez**[2], **S. A. Gamboa**[3], **P. J. Sebastian**[3, 4], and **R. Pérez**[3]

[1] Instituto de Física, BUAP, apdo. postal J-48, Puebla 72570, Mexico
[2] Instituto de Ciencias Químicas, BUAP, Puebla 72570, Mexico
[3] Instituto Mexicano del Petroleo, Programa de Investigación y Desarrollo de Ductos, Eje Central Lazaro cardenas 152, Col. San Bartolo Atepehuacan, 07730, Deleg. GAM, Mexico, D.F., Mexico
[4] Centro de Investigación en Energía, UNAM, 62580 Temixco, Morelos, Mexico

Received 30 May 2003, revised 4 August 2003, accepted 11 August 2003
Published online 10 November 2003

PACS 61.46.+w, 68.47.Mn, 72.80.Le, 72.80.Tm

We report on the improvement in electrical conductivity of Nafion® 112 membrane by the impregnation of bimetallic Au/Pd nanometric clusters. Colloidal Au/Pd nanoclusters of different molar ratios were prepared by simultaneous reduction of corresponding metal salts. The colloidal bimetallic clusters were characterized by TEM and optical spectroscopy techniques. The Au/Pd nanoclusters of different molar ratios were impregnated into the well hydrated Nafion® membranes for 3 hrs. Optical absorption spectroscopy was used to verify the impregnation process. The electrical characteristics of the impregnated membranes were investigated by electrochemical impedance spectroscopy (EIS). The experiments were performed in a solid state electrochemical cell consisted of the impregnated Nafion® in electrical contact with Au electrodes. The EIS response of the impregnated membranes showed a drastic improvement in their electrical conductivity, which promises a better performance for the proton exchange membrane fuel cell (PEMFC) when Au/Pd nanocluster impregnated Nafion® is used as solid electrolyte.

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Perfluorosulfonate ion-exchange membranes have received a considerable attention in recent years because of their application in various electrochemical systems such as electrolysis, proton exchange membrane fuel cells and gas sensors. This kind of membrane has good electrochemical properties that permit it to be used as an adequate material for conducting electricity in ionic form [1, 2]. Nafion® is a commercially available perfluorinated proton-exchange membrane developed by Dupont de Nemours Co., USA. This membrane is commonly used in electrochemical systems where the electrical transport is through electronic-ionic phenomena, those systems are for example the PEMFCs and gas sensors. Nafion® membrane provides the electric contact between anode and cathode (electrodes) taking charge of proton conduction from the oxidation to reduction reaction couple.

The electrical mechanism occurring at Nafion® and electrode surfaces is not well understood in electrochemical systems. Nafion® consists of a microscopically phase-separated structure formed by hydrophilic ionic clusters, hydrophobic perfluorocarbon backbones and an intermediate region [3-4]. The three regions interact with the electrode surface and the total charge transfer process depends on the membrane characteristics and the physico-chemical properties of the electrode [5].

[*] Corresponding author: e-mail: upal@imp.mx, Phone + 52-222295500 extn 2047

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In this study we present a novel process to obtain modified Nafion® 112 using nanostructured materials based on Au/Pd and Pd clusters for improving its electrical characteristics.

2 Experimental Bimetallic Au/Pd and monometallic Pd nanostructures were used to obtain modified Nafion® 112 membranes with improved electrical conducting properties. Au/Pd bimetallic nanostructures were prepared by simultaneous reduction of two metal ions in presence of poly(N-vinyl-2-pyrrolidone) (PVP). Ethanol solution of palladium (II) chloride (0.033 mmol in 25 ml de ethanol) was prepared by stirring dispersion of $PdCl_2$ powder in ethanol for 48 hrs. Solution of tetrachloroauric acid was prepared by dissolving crystals in water (0.033 mmol in 25 ml of water). For preparing bimetallic clusters, solutions containing two metal ions were mixed in 50 ml of 1/1 volume ratio of pure ethanol/water, 151 mg of PVP (K-30, average molecular weight 10,000) was added to the total metal ion content of 6.66×10^{-5} mol. The mixture solution was stirred and refluxed at about 100 ^{0}C for 2 hrs. For the preparation of bimetallic clusters with different Au/Pd content ratios (1/1 and 5/1), metal ion solutions of corresponding ratios were mixed in ethanol/water-PVP, maintaining the total metal ion concentration (6.66×10^{-5}) fixed, and then refluxed at 100^{0}C for 2 hrs. For the preparation of monometallic palladium clusters, 75.5 mg of PVP was added to the ethanol solution of $PdCl_2$ and refluxed for 2 hrs at 100 ^{0}C.

For Impregnation of monometallic Pd clusters in Nafion® 112 (modified membranes), Nafion® 112 membrane (by Du-Pont) was cut into 1 cm^2 pieces and hydrated as a pre-treatment procedure mentioned elsewhere [6]. The hydrated Nafion® sheets were then dipped into 10 ml of monometallic colloidal solution for 3 hrs. For preservation of the water content of the hydrated membranes, the modified Nafion® membranes were kept in plastic ampoules immersed in deionized water at room temperature. The same procedure was carried out for bimetallic Au/Pd cluster impregnation at different content ratios (1/1 and 5/1).

A JEOL-JEM200 microscope was used for the analysis by transmission electron microscopy (TEM) of the colloidal mono- and bimetallic clusters. A Shimadzu UV-VIS 3191PC double beam spectrophotometer was used for measuring the absorption spectra of the colloids. For the study of absorption spectra of the modified Nafion®, the membranes were dehydrated in a vacuum chamber. A non-modified Nafion® 112 membrane was used as reference for absorption measurements. Electrochemical studies based on cyclic voltammetry and electrochemical impedance spectroscopy were carried out with a Voltamaster4-EG&G potenciostat/galvanostat coupled to a computer interface.

3 Results and discussion Figure 1 shows the TEM micrographs of colloid clusters obtained by reduction. We can see the formation of clusters of nanometer size with average particle size varying with metal content ratios. Figure 1(a) corresponds to Pd monometallic clusters with 2.26nm average particle size. 1(b) Au/Pd bimetallic clusters with 3.5 nm average size. 1(c) Au/Pd bimetallic clusters with 5.2 nm average size. The metallic clusters obtained by reduction were used for impregnation of Nafion® 112 membrane for modifying its electrical characteristic.

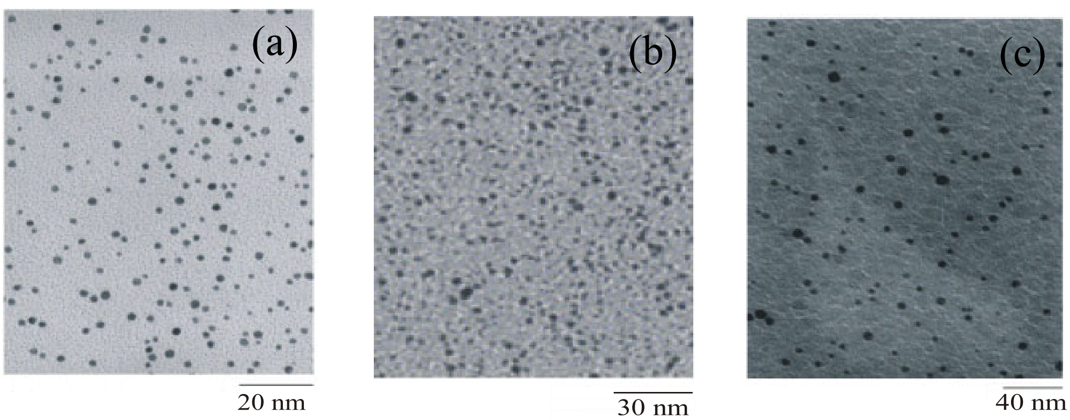

Fig. 1 TEM micrographs of colloids, (a) Pd, (b) Au/Pd(1/1), (c) Au/Pd(5/1) clusters.

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In Fig. 2(a), the absorption spectra of the bimetallic colloids with different metal content ratios are presented. The surface plasmon resonance (SPR) peak for the bimetallic nanoparticles appeared at about 530nm. There was no evidence of SPR peak below the Au/Pd ratio 5/1. In Fig. 2(b), the absorption spectra for the bimetallic cluster Au/Pd (5/1) impregnated Nafion® 112 membrane are shown. The appearance of a SPR band in impregnated Nafion® at about 560 nm for the impregnation time of 1 hr, establishes the formation of modified membranes by colloidal nanoclusters based on Au/Pd. For an impregnation time of 3 hrs the SPR peak position shifted to 570 nm and the band became broader than that for 1 hr. The same procedure was carried out for analyzing the impregnation of clusters on Nafion® 112 with other Au/Pd and Pd content ratios. 3 hrs impregnation time was considered as optimum for this study.

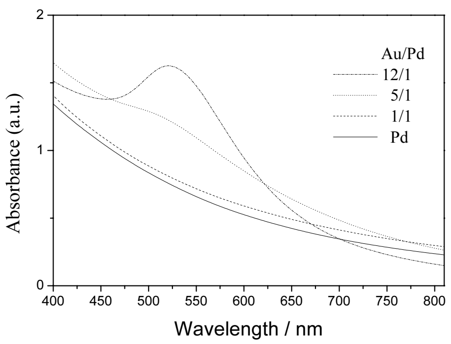

Fig. 2 a) Absorption spectra of bimetallic colloids with different metal content ratios.

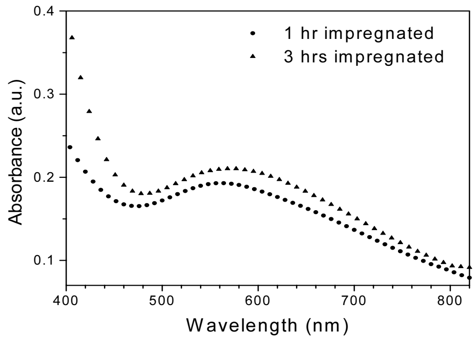

Fig. 2 b) Absorption spectra of Au/Pd (5/1) cluster impregnated Nafion membrane.

The electrocatalytic properties of metal cluster modified Nafion® 112 were investigated electrochemically by cyclic voltammetry and EIS using a related electrochemical cell in solid state configuration described by Ch. Yu et al. [7] and shown in Fig. 3.

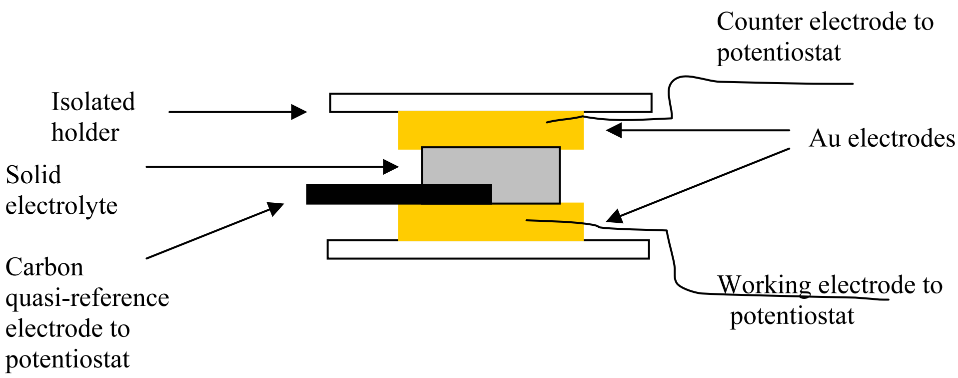

Fig. 3 Schematic representation of the solid state electrochemical cell used for characterizing modified Nafion.

Sputtered Au electrodes deposited on stainless steel sheets (0.15 mm thickness and 2 cm^2 surface area) were used as counter and working electrodes in the electrochemical cell. High purity carbon ribbon was used as quasi-reference potential. For further studies the plots can be referred to normal hydrogen electrode potential. Impregnated Nafion® 112 membranes with Au/Pd and Pd metallic nanoclusters at different metal content ratios were used as solid electrolytes. All studies were performed at constant temperature (30 ^{o}C).

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

A non-modified Nafion® 112 membrane was used as reference in electrochemical investigations. The stability of the modified membranes was made sure by monitoring the open circuit potential during the experiments.

The voltammogram plot of the non-modified Nafion® 112 for a scan rate of 10 mV/sec did not show the presence of redox reactions along the electrochemical window in the range of $-0.91 \leq$ Potential (V/ref) ≤ 0.84. For lower and upper potentials out of the range, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) took place respectively. For the case of impregnated Nafion® 112 with Au/Pd bimetallic clusters at ratio 5/1 (Fig. 4), a defined hydrogen reduction peak appeared at around 0.489 V/ref. A broad oxidation zone could be observed in anodic direction at 0.8 V/ref. The threshold potential for the HER decreased in presence of Au/Pd=5/1. It suggests that Au/Pd is acting as electro-catalyst, and we can obtain some qualitative information about the improvement in electrical characteristics of the modified Nafion® membrane. In Table 1 is presented the general results obtained for the Pd and both Au/Pd metal content ratios using characterization by cyclic voltammetry.

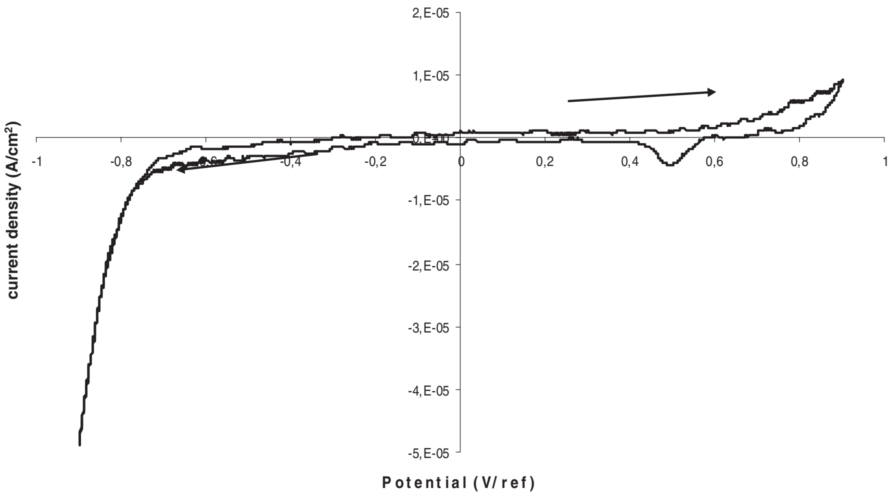

Fig. 4 Voltammogram plot for modified Nafion using Au/Pd (5/1) metallic clusters. 10 mV/sec scan rate, 30 ^{0}C.

Table 1 Resume of electrochemical parameters obtained by cyclic voltammetry of modified Nafion® 112 membranes. All potentials are referred to quasi-reference potential.

Structure (Ratio)	P_{OC}(V)	P_e(V)	P_{ads}(V)	HER threshold (V)
Nafion (non)	−0.25	−0.95	–	−0.91
Pd(1)	−0.13	−0.80	0.34	−0.77
Au/Pd(1/1)	−0.22	−0.50	0.37	−0.47
Au/Pd(5/1)	−0.02	−0.70	0.48	−0.62

Where P_{OC} is the open circuit potential, P_e is the equilibrium potential at activated H^+ scatter potential (for very low HER overpotential), P_{ads} is the adsorption potential of hydrogen in modified membranes.

From Table 1, all modified membranes showed better performance than non-modified Nafion® respect to HER threshold potential. These results mean that the electrical properties of the Nafion® 112 can be improved by using metallic clusters based on Au/Pd nanoparticles.

Electrochemical impedance spectroscopy technique was used to evaluate the improvement in electrical properties of modified Nafion® 112 membranes. The EIS spectra were recorded in the frequency range of $0.1 \leq f\,(Hz) \leq 1000$. The equilibrium potentials shown in Table 1 were used as initial potentials in EIS studies for each system.

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

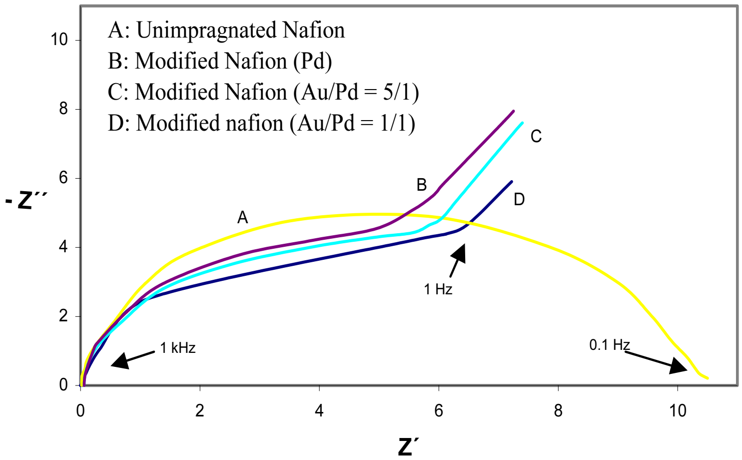

Fig. 5 Impedance spectra for colloidal metallic clusters impregnated Nafion® 112 membranes. Unimpregnated Nafion membrane impedance spectrum is used as reference.

Figure 5 shows the experimental impedance spectra for non-modified and modified Nafion membranes. The impedance spectrum of the solid state electrochemical cell with non-modified membrane (as electrolyte) is shown as fig. 5A. Its response corresponds to a polarizable device controlled by the charge transfer process between the two electrodes. The impedance responses of modified Nafion (plots B, C and D) show a decrease in the charge transfer resistance, improving the electrical characteristics of the Nafion due to the presence of metallic clusters. Adsorption and diffusion mechanisms can also be interacting with the charge transfer process in this kind of systems at low frequencies (around 1 Hz and lower). The influence of adsorption states in impregnated Nafion needs to be investigated before considering the use of these membranes in PEM fuel cell and gas sensor.

4 Conclusions Colloidal monometallic and bimetallic clusters based on Au/Pd and prepared by chemical reduction were used for obtaining modified membranes with better electrical characteristics. The use of Au/Pd based nanoclusters is capable of improving the conduction properties of membranes like Nafion®. Membranes with better electrical properties are necessary for fuel cell applications. In this work we also observed the relation between the change in HER threshold and the decrease in charge transfer resistance, as a function of the metal content ratio of the clusters. The presence of Pd and the existence of adsorption states in modified membranes need to be investigated.

Acknowledgements We would like to thank Mr. Arturo Rivera and Mr. Alejandro del Valle for their help to perform the electrochemical studies. The authors also thank to CONACyT (42146-Y) for partial financial support.

References

[1] K. Kanamura, H. Morikawa, and T. Umegaki, J. Electrochem. Soc. **150**, A193(2003).
[2] J. Maruyama and I. Abe, Electrochim. Acta, **46**, 3381(2001).
[3] P.J. James, T.J. McMaster, J.M. Newton, and M.J. Miles, Polymer **41**, 4223(2000).
[4] Z. Ogumi, T. Kuroe, and Z-I- Takehara, J. Electrochem. Soc. **132**, 2601(1985).
[5] J. Maruyama, M. Inaba, and Z. Ogumi, J. Electroanal. Chem. **458**, 175(1998).
[6] V.A. Paganin, E.A. Ticianelli, and E.R. Gonzalez, J. Appl. Electrochem. **26**, 297(1996).
[7] Ch. Yu, Y. Wang, K. Hua, W. Xing, and T. Lu, Sensors and Actuators B **86**, 259(2002).

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim