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Platinum Nanoparticles for Nanocomposite Membranes Preparation

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Abstract. This work is based on platinum nanoparticles preparation protected by a polycation- PDDA- poly (diallyldimethylammonium chloride) and to embed them in a Nafion 117 membrane matrix in order to obtain a nanocomposite structure, which can be used as alternative polymer electrolyte membrane for direct methanol fuel cells (DMFC).

Key words: direct methanol fuel cell, polymer electrolyte membrane, nanocomposite membrane.

1. Introduction

Perfluorosulfonic polymers such as Nafion are the most common electrolyte membranes in polymer electrolyte and direct methanol fuel cells due to the good thermal and chemical stability and high proton conductivity. However, methanol readily migrates from the anode, through the Nafion membrane, to the cathode, causing the significant losses of fuel, reducing open circuit potential by as much as 0.15–0.2V due to the existence of mixed potentials and poisoning the electrocatalysts on the cathode side. There is a continuing effort in the modification of Nafion based membranes in order to develop an alternative electrolyte membrane with aims to achieve low methanol permeability and high conductivity [1, 2]. One of the most common approaches is to sandwich or deposit an additional methanol-blocking thin film to Nafion membrane. Self-assembly is a well-known technique in the preparation of well-ordered nano-structures.

The design, fabrication, study and application of nanoparticle- based nanostructured films are currently intensely investigated research areas in materials chemistry [3–4]. The potential utility of such thin films includes catalysis [5–7], optics [8–10], electrics [11–12], chemical sensors [13], etc., which mainly depends on the functional properties of nanoparticle thin assemblies such as the nanoparticle type (size, shape, and composition) and surface properties, as well as the spatial distribution of the particles within the thin films.

In the last years, inorganic nanoparticles have received great interest in catalysys, magnetics, photonics and sensing.

The aim of this work is to prepare platinum nanoparticles protected by a polycation-PDDA- poly (diallyldimethylammonium chloride) and to embed it in a Nafion 117 membrane matrix in order to use this final structure as alternative electrolyte membrane for direct methanol fuel cells. The common feature of these studies is that nanoparticles with appropiate charges and surface modification in stabilized media must be prepared before film construction.

Pt nanoparticles can be prepared by alcoholic reduction in the presence of a polycation, poly (diallydimethylammonium chloride) (PDDA). Because PDDA is a positively charged ionic polymer, the PDDA-stabilized Pt nanoparticles can be self- assembled onto the Nafion electrolyte membrane, forming an electrochemically active monolayer on the Nafion membrane surface [14, 15]. Because PDDA is a strong ionic polymer, it could strongly influence the electrocatalytic properties of the platinum nanoparticles.

Polymer - stabilized metallic nanoparticles could show excellent catalytic properties and for direct methanol fuel cells applications, this type of nanocomposite polymer matrix could be a good pathway for protonic species.

2. Methods

2.1. Synthesis of polycation (PDDA) protected – Pt nanoparticles

All materials, H_2PtCl_6 – chloroplatinic acid, PDDA – poly(diallyldimethylammonium chloride) – 35 wt.% in water, MW = 5000–20 000, absolute ethanol 99.8%, NaOH (sodium hydroxide), Nafion 117 membrane were purchased from Sigma Aldrich, Germany.

Pt nanoparticles were synthesized by the alcoholic reduction of H_2PtCl_6 in ethanol/ water solution, in the presence of a polycation, poly (diallyldimethylammonium chloride) (PDDA).

In a 100 ml beaker, 50 ml of PDDA 20 mM were intensively stirring (500 rpm) while the temperature is progressively increasing, then 10 ml of 20 mM H_2PtCl_6 in ethanol /water mixture were added when the temperature achieved 80°C. The molar ratio of PDDA/ Pt was 5:1. The pH of the final solution was modified to 8.5 by adding 1 M NaOH solution. The colour of the solution changed from yellow to dark brown, indicating the platinum ions reduction.

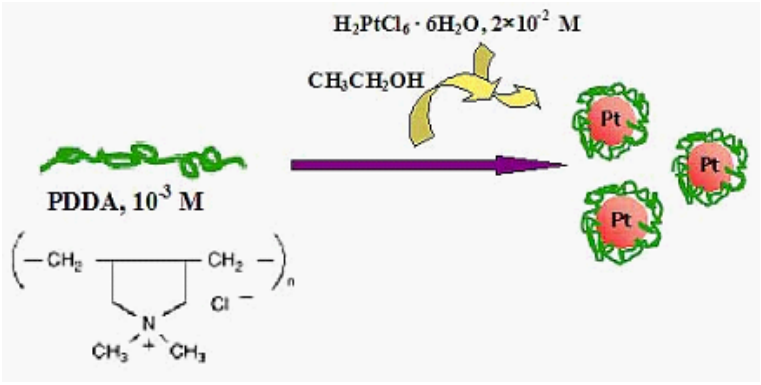

Fig. 1. Preparation of PDDA protected Pt nanoparticles.

2.2. Self-assembled structure preparation

Since the PDDA–Pt nanoparticle colloids are positively charged, they can be self-assembled to the negatively charged sulfonic acid group, SO_3^-, present on the internal surface of the Nafion membrane. This self-assembly process is governed by the electrostatic interaction.

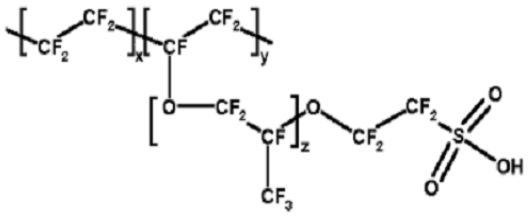

Fig. 2. Nafion structure

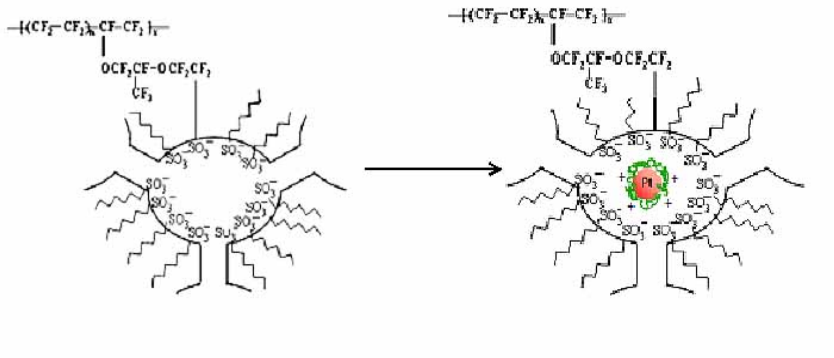

Fig. 3. Preparation of the nanocomposite membrane.

Before using, Nafion 117 membrane was treated according to the standard procedure for hydration: 30 min in a 3% H_2O_2 solution at 80°C, 30 min in deionized water at 80°C, and 30 min in a 1 M H_2SO_4 solution at 80°C. After each treatment, the membrane was rinsed in deionized water three times to remove traces of H_2O_2 and H_2SO_4. The last step was to treat Nafion membrane in a vacuum oven over night at 50°C and 50 mbars.

In order to obtain a self assembled structure, the protonated membrane was immersed over night in PDDA – Pt nanoparticles solution.

The prepared nanocomposite membrane was then analyzed using characterization methods, like, SEM, UV-vis and SAXS.

3. Results

3.1. UV-Vis characterization of the prepared PDDA-PtNP

The UV-Vis spectroscopy analyses were carried out using U-0080D Diode Array Bio-Spectrophotometer from Hitachi High Technologies.

Figure 4 shows the UV-vis spectra of the solutions containing 20 mM H_2PtCl_6, 1 mM PDDA and respectively a mixture of PDDA: Pt 5:1.

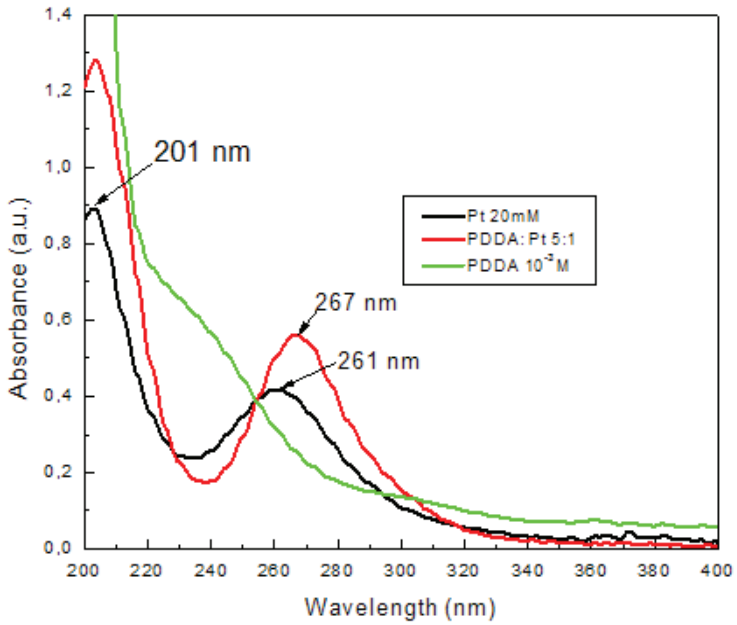

Fig. 4. UV-vis spectra of 20 mM H2PtCl6,
1m M PDDA and a mixture of PDDA: Pt 5:1.

It can be observed in the recorded spectra that while the PDDA is almost transparent on UV-vis domain, in the case of H_2PtCl_6 solution two absorbance peaks at

201 nm and 261 nm are present. There are characteristic to absorbance of platinum complex $PtCl_4^{2-}$ and $PtCl_6^{2-}$ due to the ligand to metal charge transfer transition in $PtCl_6^{2-}$ ions.

After the addition of the polycation, in the case of PDDA_ Pt 5:1 mixture, the peak from 261 nm suffers a shift to 267 nm, accompanied by an absorbance increasing, which indicates a strong coordination bond between PDDA and Pt^{4+} ions from H_2PtCl_6.

3.2. Small angle X-ray scattering (SAXS) measurements

The crystalline structure of platinum nanoparticles were investigated by X-ray diffraction methods (WAXRD- wide angle X-ray diffraction, SAXS- small angle X-ray diffraction) using a Rigaku *SmartLab* thin film 9 kW rotating anode equipped with an in-plane arm $\theta - 2\theta$ angular scanning configuration using a Cu X-ray tube, a multilayer mirror (parallel beam, X-ray K_α wavelength $\lambda_{K\alpha} = 1.540609$ Å) and an operating power of $U = 40$ kV, $I = 40$ mA, and a 2θ step of 0.05°; the contiguous X-ray emission spectra of the X-ray tube were filtered using a Ni absorber filter.

SAXS technique is very precisely for analyzing small particle used to measure a wide range of nanoparticle sizes (from 1 to several tens of nanometers).

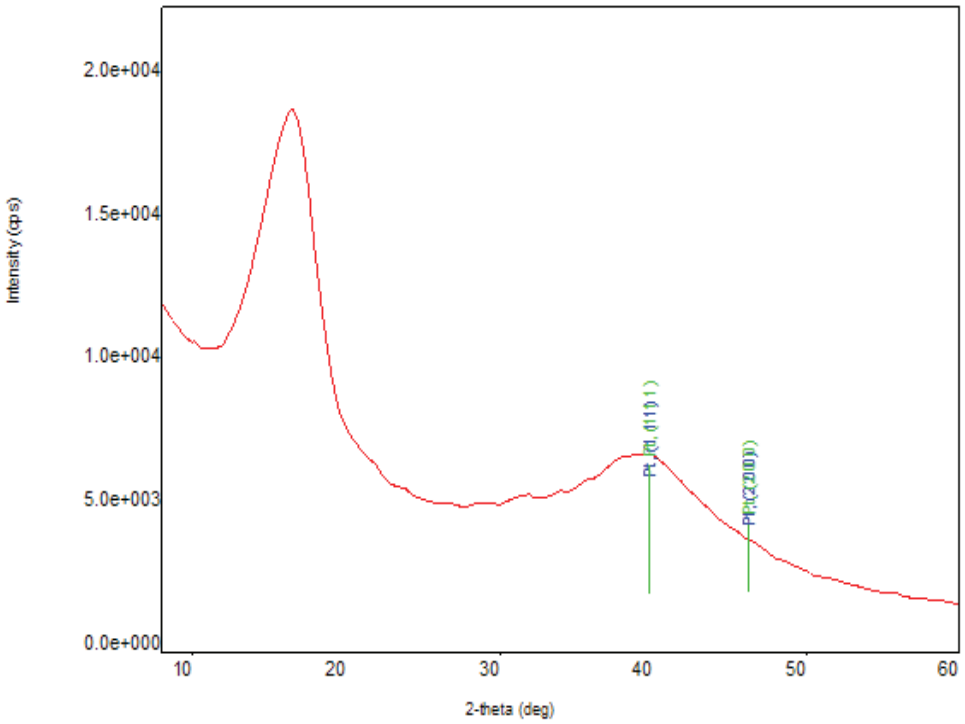

Fig. 5. XRD analysis spectrum of the prepared Nafion/ Pt nanocomposite membrane.

The diffraction peaks at 2θ of 39.2° and 42.6◦ can be indexed to (111) and (200) crystal lattice of platinum. But, the diffraction peaks at 2θ of 17° can be indexed to amorphous phase (mean crystalite size is 1–1.5 nm).

2-theta(deg)	d (A)	Height(cps)	Int. I (cps deg)	FWHM (deg)	Size	Phase name
16.71(3)	5.302(9)	8084(402)	46307 (1828)	4.32(4)	15(2)	Unknown
39.22(9)	2.295(5)	1772(188)	25385 (3886)	8.2(5)	6(2)	Platinum, syn, (1,1,1)
42.6(6)	2.12(3)	1054(145)	27605 (56533)	18(2)	3(11)	Platinum, syn, (2,0,0)

The SAXS analysis reveals the size of Pt nanoparticles as being of 3–4 nm, calculated using Scherrer equation. It can be calculated the surface area (SA) of platinum, assuming that there is a homogeneously distribution, using the following formula:

$$SA = \frac{6 \times 1000}{21.4 \times d} (\mathrm{m^2 g^{-1}}), \tag{1}$$

where 21.4 represents the density of platinum nanoparticles ($\mathrm{gcm^{-1}}$) and d is the averaged particle size (nm).

Therefore using this formula, if we consider that 3 nm is the average particle size, the $SA = 93.5\ \mathrm{m^2 g^{-1}}$.

3.3. SEM characterization of the prepared nanocomposite membrane

SEM analyses were made using the FEI Nova NanoSEM 630 system and the result reveals a 1.3 μm deposited layer on the Nafion membrane.

Before characterization, the samples were prepared by freezing in liquid nitrogen in order to observe through cross section.

The cross-section SEM images reveal the presence of the platinum nanoparticles on the membrane surface and also it is observed a modification of nafion membrane interface given by the interaction between platinum colloidal solution and nafion surface. This interface modification allows particles penetration inside the membrane. Also, it cannot be conclude the fact that there is a uniform distribution of the particles on the membrane.

4. Conclusions

The PDDA- Pt nanoparticles were successfully prepared by alcoholic reduction of H_2PtCl_6 in ethanol/ water system, using a PDDA- Pt molar ratio of 5:1 and the average size of 1.8 nm. It was also shown that the presence of the polycation- PDDA increased the absorbance of the platinum nanoparticles.

It was obtained a nanocomposite membrane using the self- assembly technique, between positively charged PDDA-Pt nanoparticles and negatively charged sulfonic acid groups SO_3^- from Nafion membrane surface, via electrostatic interactions.

The aim of this nanocomposite membrane is to block the methanol crossover from DMFC. This will be a future work to do. Also, as future work, will be parameters modification for platinum nanoparticles preparation and deposition on nafion membrane in order to obtain a uniform distribution on the surface and inside the membrane.

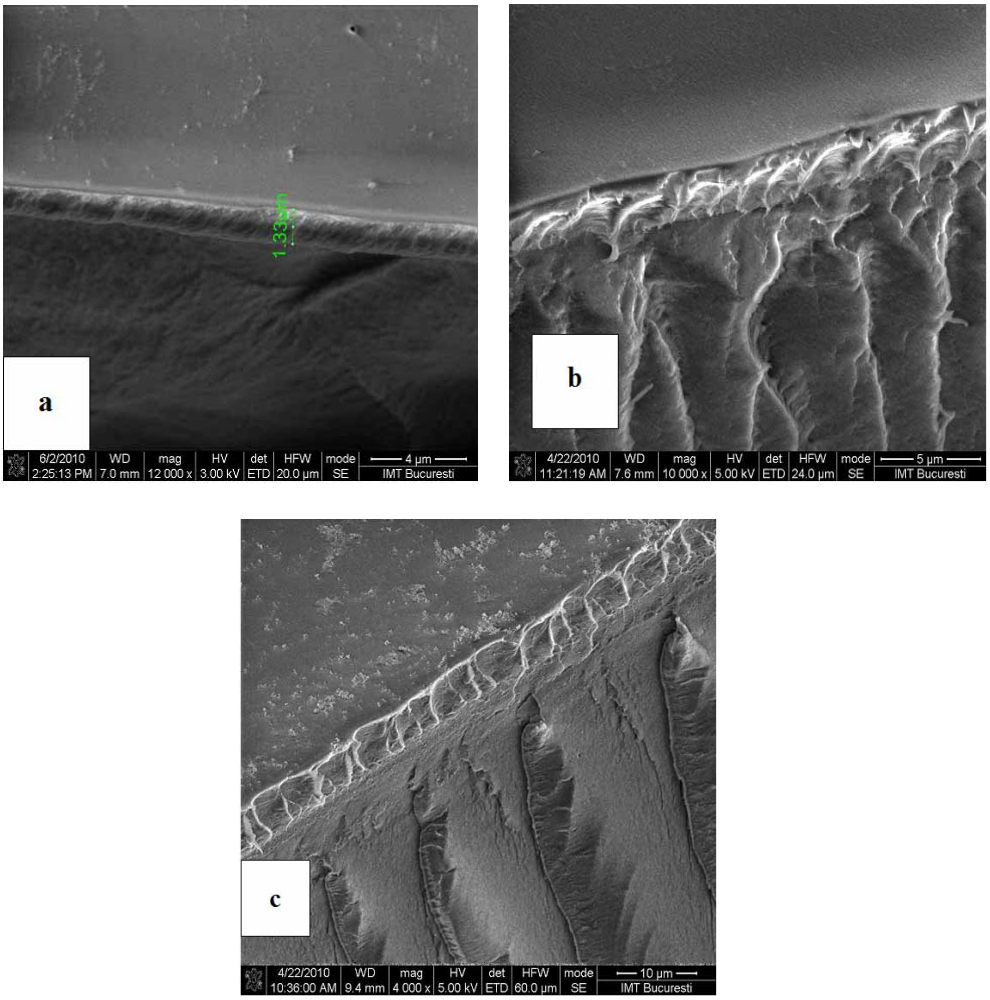

Fig. 6. (a), (b) and (c) – SEM images of the PtNP assembled on Nafion 117 membrane.

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References

[1] Aric'o A. S., Srinivasan S., Antonucci V., *Fuel Cells*, vol. **1**, **133**, 2001.

[2] Kreuer K. D., *J. Membrane Sci.*, 185, vol. **29**, 2001.

[3] Shipway A. N., Katz E., Willner I., *Nanoparticle arrays on surfaces for electronic, optical, and sensor applications*, Chem. Phys. Chem., Vol. **1**, pp. 18–52, 2000.

[4] Templeton A. C., Wuelfing W. P., Murray R. W., *Monolayer-protected cluster molecules*, Acc. Chem. Res., vol. **33**, pp. 27–36, 2000.

[5] Bond G. C., Thompson D. T., *Catalysis by gold*, Catal. Rev. Sci. Eng., Vol. **41**, pp. 319–388, 1999.

[6] Crooks R. M., Zhao M., Sun L., Chechik V., Yeung L., *Dendrimerencapsulated metal nanoparticles: synthesis, characterization, and applications to catalysis*, Acc. Chem. Res., vol. **34**, pp. 181–190, 2001.

[7] Lang H. P., Zhang H. M., Hu J. S., Guo Y. G., Wan L. J., Bai C. L., *Pt hollow nanospheres: facile synthesis and enhanced electrocatalysts*, Angew. Chem. Int. Ed., vol. **43**, pp. 1540–1543, 2004.

[8] Brighr R. M., Walter D. G., Musick M. D., Jackson M. A., Allison K. J., Natan M. J., *Chemical and electrochemical Ag deposition onto preformed Au colloid monolayers: approaches to uniformly-sized surface features with Ag-like optical properties*, Langmuir, vol. **12**, pp. 810–817, 1996.

[9] Jin Y. D., Kang X. F., Song Y. H., Zhang B. L., Cheng J. G., Dong S. J., *Controlled nucleation and growth of surface-confined gold nanoparticles on a (3-aminopropyl)trimethoxysilane-modified glass slide: a strategy for SPR substrates*, Anal. Chem., vol. **73**, pp. 2843–2849, 2001.

[10] Lu Y., Yin Y. D., Li Z. Y., Xia Y. N., *Synthesis and self-assembly of $AuSiO_2$ core-shell colloids*, Nano Lett., vol. **2**, pp. 785–788, 2002.

[11] Ogawa T., Kobayashi K., Masuda G., Takase T., Maeda S., *Electronic conductive characteristics of devices fabricated with 1,10-decanedithiol and gold nanoparticles between 1-_m electrode gaps*, Thin Solid Films, vol. **393**, pp. 374–378, 2001.

[12] Chen S., Deng F., *Rectifying nanoscale electron transfer by viologen moieties and hydrophobic electrolyte ions*, Langmuir, vol. **18**, pp. 8942–8948, 2002.

[13] Pan M., Tang H. L., Jiang S. P., Liu Z., Electrochem. Commun., vol. **7**, 119, 2005.

[14] Pan M., Tang H., Jiang S. P., Liu Z., J. Electrochem. Soc., Vol. **152**, A1081, 2005.

[15] Jiang S. P., Li L., Liu Z., Electrochem. Solid-State Lett., **8**, A 575, 2005.