

PREPARATION OF PT CATALYSTS ON REDUCED GRAPHITE OXIDE AND ITS ELECTROCHEMICAL PERFORMANCE FOR PEMFC.

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Introduction

Carbon supported electrocatalysts are widely used in PEM based fuel cells. Carbon support not only stabilizes metal particles and minimizes the use of precious metals but it should also provide mass transport of reactants to the electrocatalyst and have good electroconductivity. Different carbon materials such as single walled nanotubes, multiwalled nanotubes, graphitic nanofiber etc. have been investigated for this purpose. Renewed interest in graphite oxide opens up new route for the production of the porous carbon material with metal nanoparticles. Such materials are usually synthesized by chemical reduction or thermal treatment of the graphite oxide (GO) with adsorbed or intercalated metal complex. Chemical reduction is carried out in water suspension and results in carbon material with metal nanoparticles 10-30 nm in size [1]. Thermal treatment leads to the formation of smaller particles with average size 1-6 nm, but metal content is lower in this case [2].

In this paper we present a new method of the intercalated GO production based on cryodrying. Electrocatalyst with high metal content and nanoparticles with average diameter of 2 nm have been synthesized by thermal treatment. The sample based on cryodried GO showed better catalytic activity for oxygen reduction in PEMFC in comparison to samples based on dried GO.

Experimental

GO was prepared from the flaky graphite with a particle size of 20-60 μm according to the Hummers method [3]. The tetraammineplatinum (II) chloride used as precursor was synthesized from the hydrated hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 98 %). GO with $[\text{Pt}(\text{NH}_3)_4]^{2+}$ was prepared as follows: GO suspension in distilled water was sonicated for 15 minutes, mixed with the $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution under sonication and left for 2 hours under sonication. The $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution was prepared by dissolving of the appropriate amount of solid tetraammineplatinum (II) chloride in deionized water. The sonicated suspension was dried at 80 °C for 24 hours or by cryodrying. Cryodrying was held by VirTis AdVantage Benchtop freeze dryer. GO suspension was poured into stainless steel tray filled with liquid nitrogen. Frozen sample was dried at 10-5 bar for 24 hours; chamber temperature was varied from -30 °C to 30 °C. Dried samples were subjected to the heating at different temperatures under argon for 10 min.

X-ray powder diffraction measurements were performed on a Thermo ARL X'TRA powder diffractometer with a semiconducting Peltier-cooled detector (Cu $K\alpha_1$ radiation, $\lambda = 1.5406 \text{ \AA}$, $\theta/2\theta$ scanning mode with a step size of 0.02 °). A NETZSCH STA Jupiter 449C apparatus was used for the TG analysis. The measurements were taken in a 40-1200 °C

temperature range in a dynamic argon atmosphere (100 ml/min) at a heating rate of 10 K/min. Surface area analysis was performed with a Qsurf Surface Area Analyzer 9600. The samples were outgassed at He constant rate and 200 °C for 4 h prior to analysis. Surface area was calculated using the Brunauer, Emmett, and Teller (BET) method. Pore size distribution analysis was performed with a Thermo Sorptomatic apparatus. The samples were outgassed at 10-6 bar and 100 °C for 4 h prior to analysis. TEM investigations were performed by a JEM 2100 JEOL transmission electron microscope (LaB₆ cathode, 200 kV). Samples were prepared by casting a droplet of a dilute, aqueous suspension of the exfoliated GO on 300 mesh copper grids.

A single cell test fixture supplied by Electrochem Inc. was employed for evaluating the catalyst performance for H_2/O_2 based fuel cell. The MEA was inserted between two graphite plates, which had a serpentine flow pattern. Two Teflon gaskets of thickness 0.24 mm were introduced between the membrane and electrodes. A uniform torque of 35 in.-pounds was applied to each of the bolts used to assemble the cell. Humidified hydrogen and oxygen gases were fed into the cell at a flow rate of 200 cm^3/min and 400 cm^3/min respectively, and the cell temperature maintained at 25 °C. The current-voltage (I-V) characteristics of the cell were then evaluated. Electrocatalyst concentration was maintained at 0.4 mg/cm^2 Pt. The anode for all experiments consisted of 0.4 mg/cm^2 Pt of E-Tek carbon black-Pt. The anode and cathode catalyst films were heat pressed on Nafion 115 membrane.

Results and Discussion

XRD analysis of the dried $\text{GO}-[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ suspension (fig. 1) revealed increasing of the interlaminar distance in GO from $d_i=0,667 \text{ nm}$ to $d_i=0,713 \text{ nm}$. Obtained results were associated with the partial substitution of water molecules with the molecules of the amine complex. Interaction with the amine complex was also confirmed with TG-DSC. An exothermic DSC peak (150-270 °C), which is corresponded to the decomposition of the oxygen containing groups, transforms strongly. The "onset" temperature and reaction rate are decreased. Heat of the reaction was practically two times less as well. By the thermal treatment of the dried $\text{OG}-[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ porous carbon material with platinum nanoparticles was synthesized. Material contained small metal particles with average size 2-4 nm as well as bigger particles 50-100 nm in size.

For the cryodried $\text{GO}-[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ suspension the interlaminar distance rise to $d_i=0,844 \text{ nm}$ (fig. 1). This fact is probably connected to the modification of the intercalated layer structure. But in spite of this TG-DSC curves do not differ strongly compared to the dried samples. Thermal treatment in this case leads to the porous carbon material with platinum nanoparticles 2-4 nm in size.

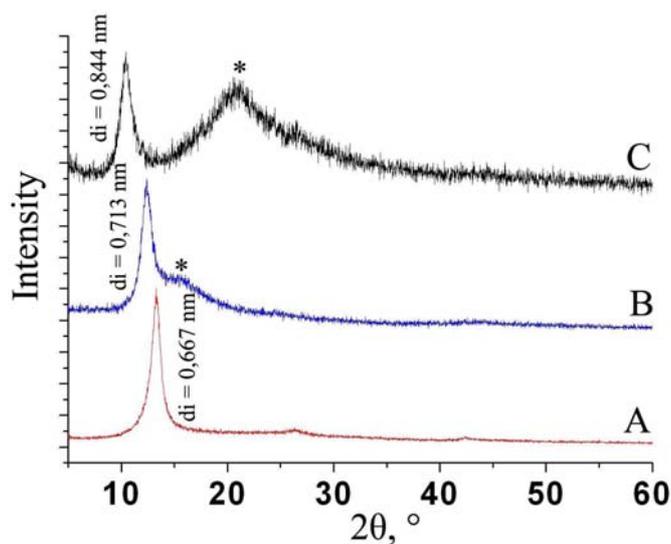


Fig. 1 XRD patterns of graphite oxide (A), dried GO-[Pt(NH₃)₄]Cl₂ suspension (B) and cryodried GO-[Pt(NH₃)₄]Cl₂ suspension (C) (* - reflection of amorphous quartz cuvette).

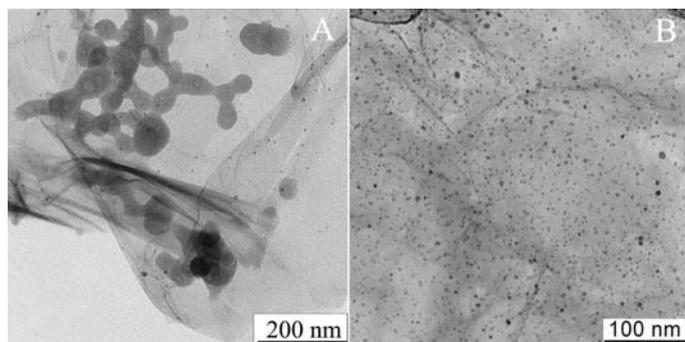


Fig. 2 TEM image of exfoliated graphite oxide with platinum nanoparticles (w(Pt) = 20 %) based on dried GO-[Pt(NH₃)₄]Cl₂ suspension (A) and cryodried GO-[Pt(NH₃)₄]Cl₂ suspension (B).

The difference between particles size is probably connected with partial redistribution of the platinum complex on the surface of GO during suspension drying. Molecules of [Pt(NH₃)₄]Cl₂ aggregate and form crystals on the surface of GO and partially on the surface of vessel. Reduction of this agglomerates leads to the platinum particles 50-100 nm in size. Compared to this complexes stabilized on the GO surface form smaller particles with average size 2-4 nm. Cryodrying preserves complex from agglomeration so after reduction only 2-4 nm platinum particles are observed (fig. 2). Owing to the large amount of surface groups anchoring metal particles, they don't agglomerate during material processing in spite of large weight content

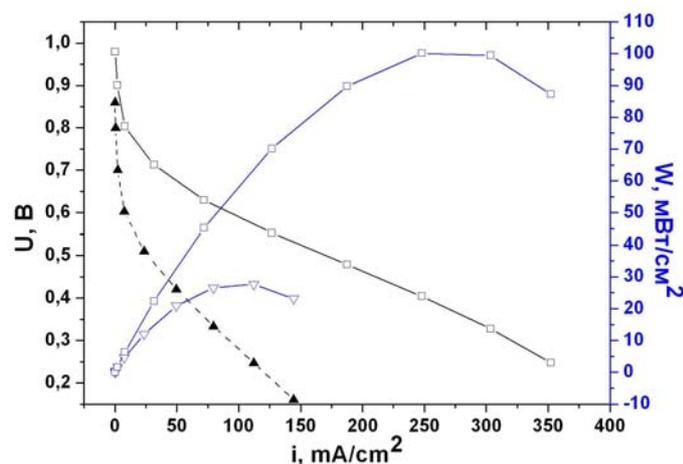


Fig. 3 Galvanostatic fuel cell polarization (I-V) curves (black) and power characteristics (blue) of a fuel cell at 20 °C and 1 atm of back pressure. The cathode was composed of dried-GO-Pt (triangles) or cryodried-GO-Pt (squares).

Cryodrying was also used for the stabilization of the GO with (Fe(Phen)₃SO₄), (Fe(OAc)₂(OH)). GO with [Pt(NH₃)₄]Cl₂ and [Ru(NH₃)₆]Cl₂ was synthesized as well. Carbon materials with Fe₃O₄ and PtFe were produced by the thermal treatment.

Proton exchange membrane assemblies were constructed using different electrocatalysts deposited on Toray paper as the cathode and Pt-dispersed on carbon black (E-Tek CB-Pt) as the anode. The performances of these assemblies in a hydrogen fuel cell are compared in figure 3.

The cryodried-GO-Pt based fuel cell delivered a maximum power of 100 mW/cm² compared to 28 mW/cm² for the dried-GO-Pt based fuel cell. Highest power was reached for the cryodried-GO-Pt after 900 °C treatment. We connect this fact with agglomeration of metal particles to the optimal size and increasing of the carbon support conductivity.

Conclusions

We offer a new approach to obtaining carbon materials with metal and metal oxides nanoparticles. It is based on extraction of OG compounds with metal complexes from water suspension by cryodrying and further thermal treatment. Material with high catalytic activity in oxygen reduction in PEMFC was obtained. Thus the method allows producing high-performance catalysts for PEM fuel-cell.

References

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