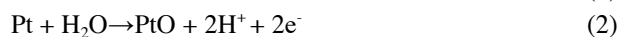


Reversible nanoparticle formation as a potential strategy for PEMFC catalyst regeneration

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Platinum nanoparticles, which are used as catalysts in Proton Exchange Membrane Fuel Cells (PEMFC), tend to degrade after long-term operation. We discriminate the following mechanisms of the degradation: poisoning, migration and coalescence, dissolution, and electrochemical Ostwald ripening [1, 2]. There are two ways to tackle this problem. The first option involves formulation of a durable catalyst, which can resist harsh fuel cell conditions, and this is the conventional route. The second option is reactivation by dissolution and then redeposition of the catalyst nanoparticles, which is an unprecedented method for the platinum catalyst regeneration and the one we shall discuss. Therefore, this work studies possibility of ex-situ regeneration of the platinum nanoparticles.

Dissolution of platinum can be achieved by potential cycling of the fuel cell electrode impregnated with platinum nanoparticles in oxygen enriched acidic electrolyte according to the following reactions [3]:



During the potential cycling platinum oxides are formed at each positive cycle and subsequently chemically dissolved as platinum ions in the electrolyte on the negative cycle. Simultaneously, direct electrochemical dissolution of platinum occurs (eq. 1). Therefore, this process is a combination of chemical and electrochemical dissolution processes. These potential cycles are alternated continuously.

The partial dissolution of platinum nanoparticles results in a decrease of the particle size and oxidation of the poisonous species on the platinum surface. The process of dissolution is monitored in-situ via cyclic voltammetry by the decay of the hydrogen adsorption/desorption peak, because the current decay is mainly caused by the dissolution of the catalyst material. The dissolution rates of platinum were significantly accelerated and controlled by temperature and chloride-ion concentration in the electrolyte (Fig. 1). More than 80% of platinum could be dissolved from the electrode. The concentration of dissolved platinum is measured with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

The next step of the regeneration procedure is redeposition of the dissolved platinum back onto the carbon support of the fuel cell electrode. This can be realized by means of the electrodeposition. A negative potential can be applied to the electrode from where platinum was dissolved to reduce the dissolved platinum ions back. So far, electrodeposition studies were performed separately in a model electrolyte on a Highly Oriented Pyrolytic Graphite (HOPG) - fig. 2. Densely and evenly dispersed on a carbon support nanoparticles (d=30 nm, h=8 nm) haven been produced. The process still needs to be optimized to obtain smaller nanoparticles. Regenerated

nanoparticles are characterized by AFM, TEM and XRD. The activity of the catalyst is studied with voltammetric techniques.

To sum up, this work studies a possibility of the regeneration of the platinum nanoparticles ex-situ on a carbon support. This strategy could afterwards be potentially applied for the in-situ regeneration of PEMFC catalysts or other carbon supported catalyst materials.

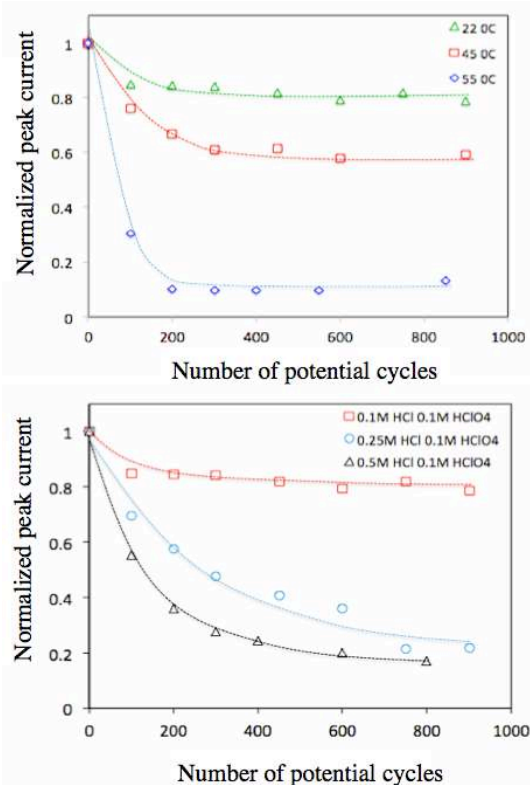


Figure 1 Cathodic peak of the hydrogen desorption at various Cl⁻ concentration in the electrolyte and various temperature.

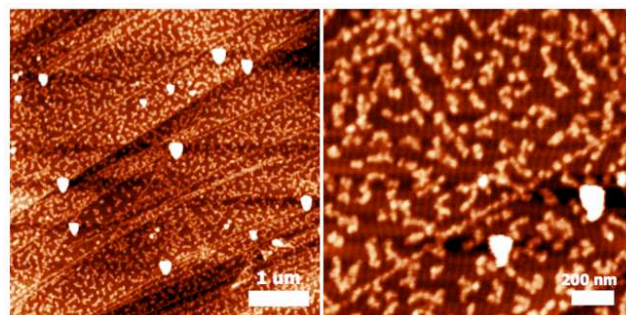


Figure 2 AFM image of platinum nanoparticles electrodeposited in 1 mM H₂PtCl₆ and 0.1M HClO₄ mixture, cathodic pulse of 0.08V for 0.2 s.

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