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Investigating the activity enhancement on Pt_xCo_{1-x} alloys induced by a combined strain and ligand effect

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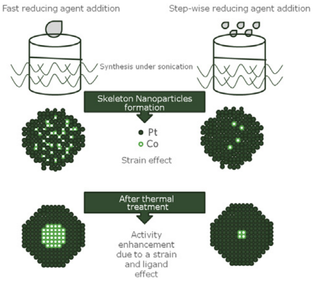
HIGHLIGHTS

- Different impregnation protocols for the preparation of fuel cell catalysts were investigated.
- The thermal treatment of Pt bimetallic alloys enhances their catalytic activity.
- The particle size distributions established by TEM and SAXS are compared to each other.
- SAXS proved to be a very useful tool for the determination of the particle size distribution.
- A combination of strain and ligand effects enhances the electrocatalytic activity of the catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to their high activity for the oxygen reduction reaction (ORR), Pt based alloys are of considerable interest as catalysts for polymer electrolyte fuel cells (PEMFC). We present two synthesis protocols that give Pt_xCo_{1-x} alloy nanoparticles (NPs) supported on a commercial carbon black support (Ketjen black EC300J) with controlled particle size, Co content and particle distribution for oxygen reduction reaction (ORR). The as prepared catalysts samples can be pre-leached in acid solution to obtain skeleton NPs and heat-treated in a reducing atmosphere to promote alloying as well as to reduce the number of low co-ordinated surface sites of the NPs. Without heat treatment, the catalysts exhibit an activity increase for the oxygen reduction reaction mainly due to a strain effect, whereas an improved performance due to a combined strain and ligand effect requires thermal treatment of the catalyst.

1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) are an alternative means for converting chemical into electrical energy. The main advantages over traditional energy converters like automotive engines are the higher conversion efficiency as well as the fact that – if hydrogen from a renewable source is used as fuel – the only product is pure water. However, applications like automotive transport demand the reduction of the cost of fuel cell catalysts, which can in part be achieved by reducing the amount Pt used in the catalyst layer. A more cost effective solution as compared to pure Pt would be alloying Pt with a transition metal (Ni, Co, Fe etc.). For this reason, recently Pt_xCo_{1-x} alloys have attracted considerable

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interest as catalysts in PEMFCs due to their superior electrocatalytic properties over Pt for catalysing the Oxygen Reduction Reaction (ORR) [1–4]. The main aim in replacing Pt by Pt-alloys is to decrease the amount of Platinum used in the catalyst in order to alleviate its high cost, but also to increase the reaction rates (activity) and thus enable higher power densities for automotive applications [5].

A variety of techniques are being used for the synthesis of carbon supported Pt alloy NPs, with the most common ones being the impregnation (precipitation) approach [6], which was used for this work, and the incipient wetness approach [7]. The latter is a specific impregnation technique, whereby the active metal precursor is dissolved into a suitable solvent and then contacted with a specific amount of support (high surface area carbon). The essential characteristic is that the volume of the dissolved precursor equals the pore volume of the carbon support. Capillary action then draws the solution into the pores of the support until they are fully saturated, after which the carbon support material begins to appear incipiently wet. A number of processes including selective adsorption, ion exchange and polymerisation/depolymerisation may take place. Then the product is dried and heated (calcined) to remove any excess solvent and decomposes the metal salts into metal oxides. Finally the catalysts may be reduced to convert the metal oxide [8].

The impregnation (precipitation) technique used here is similar to incipient wetness technique, however, an excess of solvent is used during the synthesis, which renders the process slow, because the metal deposition becomes a diffusion process, which is much slower than the capillary one. In order to increase the reaction rate and to convert the metal salts into metallic NPs, a reducing agent (e.g. $NaBH_4$) is typically introduced. Therefore the particle formation involves two distinct processes, namely nucleation (seed formation) and growth. Nucleation requires that the system is far from equilibrium, i.e. high supersaturation or for ionic species a solubility product far exceeding the solubility constant of the solid to be precipitated. Growth of the new phase takes place during conditions which gradually approach the equilibrium state. After synthesis, the excess solvent is separated from the catalyst (precipitate), e.g. by centrifugation. Finally the as prepared catalyst can be further heat treated to decompose any remaining organics and in the case of alloys, to enhance the alloying. Alternatively, a colloidal approach can be used, where Pt or Pt-alloy NPs are preformed in a colloid solution and later attached to the support [9].

Synthesis of Pt_xCo_{1-x} alloy Nanoparticles (NPs) by using an impregnation method can yield NPs with high ORR activity and tunable Pt content as well as particle size [10–13]. Moreover, leaching of the excess surface Co roughens the surface of the NPs leading to a Pt-skeleton surface [1,2]. Heat treatment of the NPs increases the particle size, but can also induce Pt segregation to the surface and the formation of Pt(shell)–Co(core) structures. A strain effect [14] induced from the particle core to the Pt shell can further increase the activity of the catalyst [15].

While all these effects are widely discussed, it is not exactly known how variations in the synthesis protocol influence these effects in a controlled manner and thus allow a fine-tuning of the catalytic behaviour of the catalyst. The knowledge of which approach leads to optimized results is mainly based on trial and error and largely descriptive. In this work we therefore focused on how variations of impregnation – a traditional synthesis method – affect these parameters on carbon supported Pt_xCo_{1-x} NPs. In particular, we studied the manner in which acid leaching and heat treatments change the particle composition and enhance the activity.

2. Experimental

For the synthesis of carbon supported Pt_xCo_{1-x} NPs, 0.052 mmol of K_2PtCl_4 and 0.052 mmol $CoCl_2 \cdot 6H_2O$ were dissolved in 5 ml Ethylene Glycol (EG) each. Then the solutions were ultrasonicated and purged with Ar to remove any oxygen traces. 40 mg of EC300J Ketjen black (Akzo Nobel) high surface area carbon support was added to 10 ml of EG and ultrasonicated to disperse the carbon powder under Ar flow while the pH of the solution was increased to 10 by the addition of NH_4OH. Subsequently, a very small amount (0.2 ml) Pt precursor and 2 ml of a freshly prepared 0.1 M solution of $NaBH_4$ as a reducing agent were added to the carbon suspension under sonication in order to reduce the Pt precursor and form Pt seeds. After 2 min the remaining Pt and Co precursor solutions and a freshly prepared 10 ml solution of $NaBH_4$ were added to the suspension. This method will in the following be denoted as method I. In method II, instead of adding the remaining Pt and Co precursor as well as the $NaBH_4$ solutions at once after the seed formation, the solutions were added in a stepwise fashion until all the Pt and Co precursors were used. In detail, after the seed formation, 1 ml of the Pt and Co precursor solutions were added drop wise to the carbon suspension within a few seconds, followed by the addition of 2 ml of 0.1 M $NaBH_4$ solution. After 2 min of reaction and sonication, this procedure was repeated for another 4 times until all the Pt and Co precursor solutions and the $NaBH_4$ solution were used. Sonication was used through the whole catalyst synthesis procedure. Finally, the catalyst suspension was further sonicated for 2 h under Ar flow. The final product was fine black powder with 20 wt. % Pt loading.

The untreated catalysts were copiously washed with water, these catalysts will be denoted as unleached/PtCo/C(I) and (II) respectively. In the cases denoted as leached (leached/PtCo/C), the as-synthesized catalyst was centrifuged and washed in HCl to remove the excess ethylene glycol and to leach out the surface Co from the NPs. Optionally the leached catalysts were heat treated (HT) in reducing atmosphere (4%H_2–96%Ar) at 500 °C for 30 min, to enhance the alloying and reduce low-coordinated surface sites, denoted as leached/HT PtCo/C(I) and (II).

The electrochemical characterization of the catalysts was conducted in a three-electrode electrochemical cell with a glassy carbon (GC) rotating disk electrode (RDE, 5 mm in diameter) as a working electrode (WE), a Pt-mesh as the counter electrode (CE), a Saturated Calomel Electrode (SCE) as reference electrode (RE), and a home-build potensiostat [16,17]. In order to obtain a thin catalyst film on the GC WE the catalyst powders were dissolved in Millipore water and a known quantity of catalyst ink was pipetted onto the GC electrode, to obtain a Pt loading of 14 μg_{Pt} cm^{-2}. Thereafter the ink was left to dry on the GC electrode under a N_2 stream. As in our previous work, no Nafion binder was necessary for the catalyst ink to adhere on the GC electrode, since no catalyst was visibly detected in the electrolyte solution after the electrochemical measurements. During the electrochemical measurements, the WE potential was compensated for the IR drop to obtain a residual resistance of less than 3 Ω. All potentials are given with respect to the reversible hydrogen electrode (RHE) potential, which was experimentally determined before each measurement series.

The oxygen reduction reaction (ORR) activity was determined in 0.1 M $HClO_4$ prepared from Millipore® water (>18.3 MΩ cm, TOC < 5 ppb) and $HClO_4$ (Merck suprapur). The measurements were performed at room temperature. Prior to the measurements the electrolyte was de-aerated by purging with Ar gas (99.998%, Air Liquide), and the measurements were started with cleaning the catalyst by potential cycles between 0.05 and 1.1 V_{RHE} at a scan rate of 50 mV s^{-1}. The specific activity of the ORR was determined in accordance to our previous work [18] from the positive going RDE polarization curves recorded in O_2 saturated 0.1 M $HClO_4$ solution at a scan rate of 50 mV s^{-1} and at a rotation speed of 1600 rpm. The polarization curves were corrected for the non-faradaic background by subtracting the CVs recorded in Ar-purged electrolyte.