



Surface and electrochemical characterisation of a Pt-Cu/C nano-structured electrocatalyst, prepared by galvanic displacement

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ABSTRACT

A two-step procedure at room temperature was applied to prepare a bimetallic Pt-Cu carbon-supported catalyst (Pt-Cu/C). First the chemical reduction of Cu ions by sodium borohydride in the presence of Vulcan XC72R carbon powder is performed. Second, the partial galvanic replacement of Cu particle layers by Pt is achieved upon immersion in a chloroplatinate solution. The characterisation of the Pt-Cu/C catalyst by XRD and XPS proves the formation of Pt-Cu alloying. The electrochemical active surface area (EASA) is determined for the Pt-Cu/C transmetalation catalyst as well as for a commercial Pt/C catalyst from the Alfa Aesar HiSpec[®] product line. The resemblance in surface voltammetry is an indication for a Pt rich shell. The catalytic activity towards the oxygen reduction reaction for both catalysts is evaluated by using linear sweep voltammetry (LSV) in combination with a rotating disc electrode. Koutechý–Levich analysis shows that the Pt-Cu/C catalyst has a higher catalytic activity towards the oxygen reduction reaction (ORR) at 0.8 V and 0.85 V vs RHE compared to the tested commercial catalyst. The activity increase is attributed to a “ligand effect”-modification of the core metal on the Pt shell.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) provide a promising link in the future sustainable energy cycle. Zero emission vehicles as well as stationary fuel cell systems are already in the development stage. The major disadvantage today is the higher capital cost compared to conventional electricity production methods [1,2]. The performance of the cathode electrocatalyst in PEMFC's is of paramount importance due to the sluggish electroreduction of molecular oxygen to water at the cathode side. The fairly strong Pt-O surface bond is believed to lie at the basis of the slow oxygen reduction reaction (ORR) kinetics [3]. Unsupported or carbon-supported pure Pt materials are the most widely used cathode electrocatalysts during the last decades [4]. Alternative catalyst materials could dramatically decrease the capital cost through an increase in catalytic activity—resulting in higher fuel cell (FC) efficiency—or through a lower Pt content. Two strategies

are deployed in the search for more active ORR electrocatalysts; on one hand lowering the Pt amount in Pt-M alloys [5–8] and on the other hand the search towards non-Pt catalyst concepts [9–11].

Over the years several Pt-M alloy catalysts have shown to significantly increase activity towards ORR due to the alloying effect [12]. Amongst them, Pt-Pd and Pt-Co alloy catalysts were extensively studied [13,14]. The alloying augments the surface area-based activity as well as the Pt mass-based activity. Especially from an economic point of view the latter provides a good basis to benchmark FC electrocatalysts. Where the surface area based activity significantly increases, the Pt mass based activity undergoes only a rather small attenuation leading to an almost equally expensive catalyst. The solution to this problem is brought by controlling the nanoparticle morphology to form core-shell structures. As little as a few monolayers of the shell metal can be deposited on an alloyed or single metal core. Consequently the mass based activity is drastically increased.

High temperature annealing is frequently applied in order to segregate Pt-M alloyed nanoparticles into a core-shell structure. Despite the increase in specific activity, particle sintering causes a dramatic decrease in electrochemical surface area (ECSA) [15,16]. Wei et al. reported the electrodeposition of Cu nanoparticles on porous carbon electrodes [17]. Even though this technique enables

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an effective use of noble metal catalysts due to exclusive deposition on accessible electrode regions, minimum particle sizes remain 20–70 nm. Electroless methods on the other hand have the advantage of creating nanoparticles in the 2–5 nm diameter range. Fine tuning the nanoparticle morphology to create a core–shell structure can be done by electrochemical [4] or chemical [18] leaching of the core metal or through the deposition of an additional metal layer [19].

An alternative method for the preparation of multimetallic catalysts has been developed, based on the spontaneous replacement of an initially deposited less noble metal by a more noble one, a process often termed galvanic replacement or transmetalation [20,21]. It was first applied by Adzic and co-workers [22–25] for the complete replacement of Cu UPD monolayers by Pt, Pd or Ag and then by a series of noble metals or their mixtures. Kokkidinis and co-workers [26,27] applied the technique to the partial replacement of electrodeposited Cu and Pb polylayers by Pt (resulting in Pt shell–Cu or Pb core particles). This approach has been recently further developed by Sotiropoulos and co-workers who prepared Pt–Cu, Pt–Pb, Pt–Fe, Pt–Co, and Pt–Ni binary catalysts by the transmetalation process and tested them with respect to their activity towards oxygen reduction [28,29] and hydrogen evolution [30]. This technique has been taken to the next step by preparing core–shell Pt–Cu nanoparticles on a porous carbon support [20,31,32]. The simple replacement reaction between the Cu nanoparticle catalyst and a Pt salt not only provides better control of morphology, but also presents a low cost production method for porous carbon deposited nanoparticle FC catalysts [32].

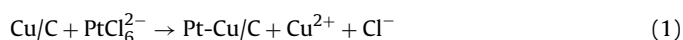
It was found recently that model Pt/Cu electrodes, prepared by the transmetalation of Cu layers on glassy carbon [30] and their particle analogues prepared from Cu particles on Vulcan XC72R carbon support [33] exhibited higher medium-term activity towards methanol oxidation. Based on these findings the aim of this work is to assess the electrocatalytic activity of Pt–Cu/C powder catalysts towards oxygen reduction reaction in comparison with a commercial Pt/C catalyst with similar Pt loading. The continuation of the two-step method as an alternative route for the preparation of practical Cu@Pt catalysts is used. Due to the ease for Cu to form oxides in neutral and basic media only few authors reported on the galvanic replacement process with Pt [34]. As a result many hiatuses still remain in the formation of the supposed core–shell structure. The obstacles of Cu@Pt nanoparticle formation will be overcome in this work through applying the two-step galvanic replacement process. Formation, properties and ORR activity of the synthesised Cu@Pt nano-structured catalyst will be evaluated. Surface characterisation techniques such as EDS, TEM and XPS will be combined with the electrochemical characterisation using linear sweep voltammetry (LSV) in combination with rotating disc electrode (RDE). Special attention will be devoted to H UPD measurements since intrinsic catalytic activity as well as the practical application of the catalyst is indicated by the electrochemical active surface area (EASA).

2. Experimental

2.1. Preparation of a Cu@Pt transmetalation catalyst [33]

The support for the catalyst is high surface area carbon black powder (Vulcan XR 72, Cabot), a typical substrate used in fuel cell environments. To activate the carbon powder it was exposed to an oxidative pretreatment, leading to an increased number of the functional groups on the surface [35]. For this purpose 0.25 g carbon black (Vulcan XC72) is treated with a 1 M sulfuric acid and 10% (w/v) ammonium persulfate solution during 24 h of magnetic stirring at room temperature. The obtained suspension is then filtered, and the precipitate is rinsed with distilled H₂O and left to dry

overnight. The oxidised carbon is mechanically ground in a mortar and suspended in 90 ml water. Then a two-step catalyst preparation procedure is applied. First the carbon powder is impregnated with an ionic solution of the non-noble metal, prepared by dissolving 0.4 g CuSO₄ · 5H₂O (0.1 g Cu or 0.0016 g-atom of Cu; Sigma–Aldrich (ACS reagent)) in 10 ml water and adding it to the carbon suspension. Maximum copper ion adsorption on the carbon surface is ensured by magnetically stirring the preparation during a 24 h period. To reduce the adsorbed Cu(II), a 1 M NaOH solution containing 12.8 ml (0.0128 mol) of 0.1 M NaBH₄ is added to the suspension (an excess of reducing agent is created). The resulting suspension is stirred in an ultrasonic bath for 30 min and filtered afterwards. Second, the obtained Cu/C precipitate is left to dry in air and is then slowly added under continuous stirring to 50 ml of 10^{−2} M K₂PtCl₆ solution containing 0.1 M HCl for the electroless platinisation to occur:



The reaction mixture was stirred in the ultrasonic bath for another 30–45 min, filtered and left to dry in air. With this nanoparticle powder the catalyst inks were prepared and coated on the glassy carbon electrodes for further electrochemical tests. The developed Pt–Cu/C nano-structured catalyst is benchmarked to a well-known commercial Pt nanoparticle catalyst. This commercial catalyst from the Alfa Aesar HiSpec[®] catalyst line (product number 35849) is optimised for usage in fuel cells and is supported on a porous carbon black substrate. The chosen metal loading of this catalyst is 20 wt%, comparable to the Pt loading in the Cu@Pt catalyst.

2.2. Microscopic, spectroscopic and crystallographic characterisation

Transmission electron microscopy (TEM) was carried out using a Philips M20 TEM system. Energy Dispersive Spectroscopic (EDS) elemental analysis was performed using the utility of a JEOL JEM 6390/EDS system. X-ray Diffraction patterns of the catalyst powders were obtained using Cu anode–WL1 K α filtered radiation ($\lambda = 1.5406 \text{ \AA}$) and scintillation registration with a constant scanning step $\delta(2\theta) = 0.02^\circ$, and a counting time per step of 3 s. X-ray photo electron Spectroscopy (XPS) studies were performed in a PHI model 1600 system equipped with an Omni Focus Lens III using a standard Mg K α X-ray source at a high voltage of 15 kV, 300 W. The PHI Multipak 8 software was used for data interpretation.

2.3. Electrode preparation and electrochemical characterisation

Electrochemical experiments are done in a three-electrode electrochemical cell using a Ag/AgCl reference electrode with a Luggin capillary and a Pt wire counter electrode. A 0.5 M H₂ SO₄ electrolyte solution is used. The glassy carbon working electrode (0.6 cm diameter) is coated prior to the tests with the catalyst ink, consisting of a suspension of the catalyst powder in a 50:50 water isopropanol mixture. The catalyst inks were sonicated for 2 hours to ensure a homogeneous suspension. Using a micro pipette, 5 μl of the catalyst ink is applied at the glassy carbon surface resulting in a catalyst coverage of 15 $\mu\text{g}/\text{cm}^2$. After the electrodes have dried to the air at room temperature for roughly 15 min a thin perfluorosulfonic acid (PFSA) layer—also known under the commercial name Nafion[®]—is applied by adding 10 μl of 5% PFSA solution in 50:50 water–alcohol solvent. This layer acts as a binder for the catalyst powder to produce mechanically stable electrodes while assuring the proton transport towards and from the active surface.

CV measurements are obtained using a Biologic VSP-300 potentiostat equipped with an analogue scan generator. The LSV measurements are performed using an Autolab PGSTAT 302F in combination with a Radiometer EDI101 rotator.

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