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Enhanced oxygen reduction and methanol oxidation reaction activities of partially ordered PtCu nanoparticles

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Abstract

Platinum copper alloy nanoparticle catalysts supported on graphitized carbon with and without partial crystal ordering were synthesized and tested for oxygen reduction and methanol oxidation reaction for potential use in direct methanol fuel cells and proton exchange membrane fuel cells. The activity enhancement by at least a factor of 2 is possible when Pm-3m phase is present in the nanoparticle with respect to the pure Fm-3m phase. A significance of Pt-skin type catalysts concept is explained for lowering the platinum content.

1. Introduction

The efficiency of the PEM fuel cell is mostly dependent on the increase in the activity of the cathode catalyst for oxygen reduction reaction (ORR) where large voltage losses are still not resolved [1]. For now it seems that only platinum based catalysts show the satisfactory performance for the required efficiency

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that could potentially lead to the commercialization. The enhancement of oxygen reduction reaction (ORR) activity of Pt alloy over pure platinum catalyst has been well studied over the years by many acknowledged research groups [2, 3, 4, 5, 6, 7, 8, 9, 10] from which a common conclusion can be drawn: more active Pt alloy surfaces possess altered electronic structure that favours a faster ORR kinetics. Additionally, on pure Pt the anode methanol oxidation reaction (MOR) also shows relatively sluggish kinetics [11] that needs to be appropriately addressed. The most studied Pt alloy used for MOR has been PtRu/C which makes the reaction run with the bifunctional mechanism [12], that is, with the help of "reactant-pair" mechanism originally proposed by Gilman in 1964 [13]. For the Pt alloys whose non platinum component is not stable in acid (Ni, Co, Cu, … [14]) there are papers reporting a high MOR activity, presumably due to a lowered CO adsorption energy if compared to Pt [11, 15, 16].

One of the many remaining questions in Pt alloy fuel cell catalyst is whether we can further increase the activity by varying various parameters, such as structural ordering [17] etc. By ordering we mean the presence of intermetallic compounds with ordered distribution of two or more metals that give additional diffraction peaks in the XRD spectra. It has already been shown that the activity of Pt based catalyst could be altered by change in the degree of structural ordering [18, 19, 20, 21, 22].

Since the mass activity is a product of specific activity and the electrochemical surface area (ESA), and is probably the most influential parameter in the production of the fuel cells, we explain and stress the importance in understanding of the well known concept of core shell and platinum monolayer catalyst [23].

In this paper we show a twofold enhancement in specific activity in ORR and in MOR of the ordered PtCu/C catalyst over the disordered one and a ninefold enhancement in ORR over a Pt standard (fivefold in MOR). We clarify the concept of enlarging the ESA with monolayer type catalyst that is size independent and hence particle size effect independent.

2. Experimental

A PtCu/C catalyst was synthesized according to the procedure described in our recent patent application [24]. The atomic ratio of Pt:Cu is 1:3 and the catalyst composite contains about 60 wt.% of Vulcan 72-XC carbon support. The Pt/C standard has about 29 wt.% Pt content (average particle size 4 nm).

Different degree of ordering was achieved with the same precursor PtCu/C catalyst by adjusting the annealing program procedure. To obtain the catalyst with disordered structure, i.e. random distribution of Pt and Cu atoms, the temperature was set above the order-disorder transition temperature obtained from the phase diagram [25] and then quenched, so the solid solution was obtained. Catalyst with ordered structure, i.e. non-random alternating Pt and Cu distribution, was obtained by setting the temperature below the order-disorder transition temperature for certain time so that the system attained thermodynamic equilibrium. Since the same precursor was used for the partially ordered and the disordered catalyst the same Pt:Cu atomic ratio and the same particle size distribution is obtained. The latter variables are thus excluded as variables decisive for the differences in activity of these two catalysts.

The qualitative and quantitative X-ray powder diffraction analysis of the collected XRD patterns was performed using the Crystallographica Search-Match programs [S-XRD1] and TOPAS V2.1 Rietveld refinement program [S-XRD2]. X-ray powder diffraction patterns for the analysis were collected at room temperature on a laboratory PANalytical X'Pert PRO diffractometer using CuKα1 radiation (1.54060 Å). The samples were loaded into a flat disc-like sample holder. The XRD data were collected in the 2Θ range from 5 to 140º in steps of 0.008º 2Θ with a total measurement time of 16 hours. In the Rietveld

refinement of different alloys, phases with Fm-3m and Pm-3m symmetry were taken into account. In the Fm-3m phase a random distribution of Cu and Pt over the (0,0,0) site was assumed. In the Pm-3m phase Cu was occupying the (0,½,½) site and Pt or Cu the (0,0,0) site. The diffraction peaks profiles were approximated using Double-Voigt approach. The refined parameters in the final cycle of all refinements were 8 background polynomial parameters, zero shift, absorption correction, and for each phase lattice parameters, scale factors, microstrain and crystallite size. Chemical composition was determined by EDS. [S-XRD1] Crystallographica Search-Match, version 2,1,1,0, Oxford Cryosystems, UK, 2003. [S-XRS2] TOPAS V2.1, Users Manual, Bruker AXS, Karlsruhe, Germany, 2000.

Rotating disk electrode (RDE) measurements were performed in a thermostated standard two-compartment electrochemical cell (V = 50 mL), using a glassy carbon disc electrode (A = 0.196 cm2, Pine Instruments) with a potentiostat (ParStat 2273, Princeton Applied Research) and rotation control (MSRX speed control, Pine Instruments). A silver/silver chloride reference electrode (SSCE, BASi), separated by an electrolytic bridge from the main cell compartment, was used, however, all potentials are given with respect to the reversible hydrogen electrode (RHE). A Pt wire was used as counter electrode. Supporting electrolyte was 0.1 M perchloric acid (70%, pro analysi, Merck) prepared using Milli-Q filtered (Millipore) water. For the thin-film RDE (TF-RDE) measurements, carbon-supported catalysts were drop casted on polished glassy-carbon disks by applying 20 µl of a well-dispersed catalyst in water ink (1 mg/ml). After evaporation of water in nitrogen (Messer, 5.0) stream at room temperature, catalyst loadings ranged between about 20 $\mu gPt/cm^2$ for PtCu/C and 30 $\mu gPt/cm^2$ for Pt/C catalysts. To stabilize the catalyst particles on the substrate, 3µl of a Nafion® (5wt.%, Fluka) and isopropyl alcohol (pro analysis, Merck) 1:50 mixture was pipetted onto the disc. The electrochemical characterization began with 90 cycles between 0.09 and 1.19 V versus RHE in order to obtain a stable cyclovoltammogram. Oxygen reduction activities were measured at 1600 rpm, 25 °C, in solution saturated with oxygen (Messer, 5.0), at a sweep rate of 20 mV/s in the same potential window. Electrochemically active surface areas were determined by CO-stripping and hydrogen underpotential deposition (Hupd). At the end the methanol was added and MOR was measured with a sweep rate of 50 mV/s. The correction for the uncompensated ohmic resistance was applied (cca. 20-25 Ohm) [26]. The iR drop between the reference and working electrode was obtained with the fast impedance measurement at 0.35 V versus RHE in 1 M MeOH and 0.1 M HClO4 at room temperature (amplitude 0.01 V and range 1 Hz to 10 kHz). With MOR this is even more obvious than in the case of ORR, because the peaks are not symmetrical if the compensation is not correct. This is because of higher current densities due to higher concentration in the case of methanol (1 M) than in the case of oxygen (concentration around 10^{-3} M). One can also estimate whether the correction made is right, since in this case the methanol peaks become symmetrical (they are not shifted to higher potential anymore). RHE measurements were done with platinum disc electrode (A = 0.196 cm^2, Pine Instruments), which was placed in 0.1 M perchloric acid solution saturated with hydrogen (Messer, 5.0), rotated at 1600 rpm and measured at the open circuit potential. The latter was shifted by -0.29 mV with respect to SSCE.

3. Results

XRD spectra of the two catalysts are shown in the Figure 1 a. At the diffraction angles of about 24 and 34 2Θ two additional peaks appear characteristic for the ordered phase in PtCu/C catalyst. This is known to be the Pm-3m phase (Figure 1b), whereas other peaks belong to the solid solution phase with random distribution of atoms (Fm-3m shown in Figure 1c) which is present in both catalysts. The phase composition is roughly 1:1 (Pm-3m:Fm-3m).
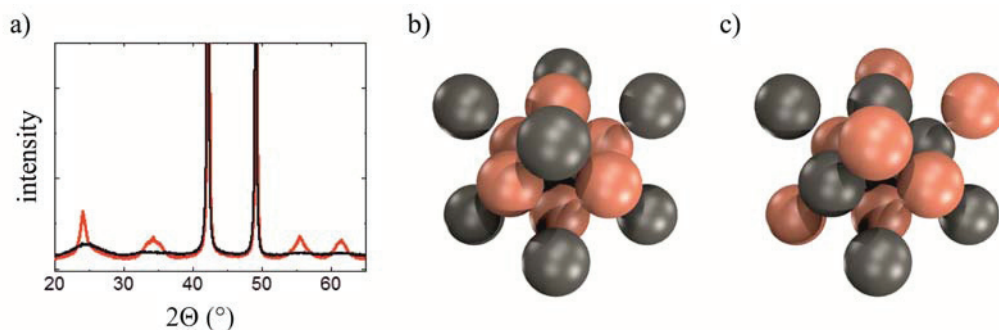

Figure 1. a) is a XRD of PtCu/C catalyst (black is disordered and red is ordered) and two atomic arrangement of PtCu/C catalyst (gray spheres represent platinum atoms and red spheres represent copper atoms): b) represents ordered and c) represents disordered phase.

The oxygen reduction reaction (ORR) polarization curves (Figure 2a) were measured at similar conditions for the correct comparison. We can deduce from the Tafel slopes at 0.9 V in Figure 2b that the ordered PtCu/C catalyst gives the highest ORR specific activity. Disordered PtCu/C activity is about twice lower, whereas the Pt/C catalyst is about 9 times less active (Figure 2c). A similar trend is observed from the peak currents of methanol oxidation reaction (MOR) positive polarization sweeps (Figure 3a and b). It should be noted that the MOR was measured on the same catalyst films and in the same electrolyte as ORR.
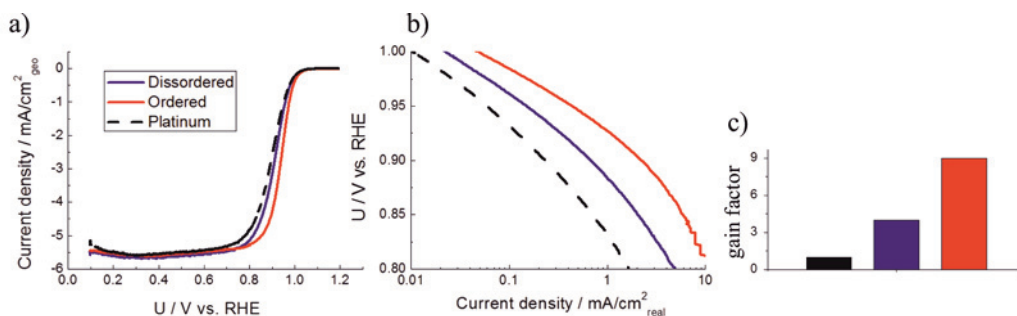

Fig. 2. a) ORR polarization curves in 0.1 M HClO4 at rotation of 1600 RPM with 20 mV/s of Pt/C and two PtCu/C catalysts (black is platinum, blue is disordered and red is ordered), b) are Tafel plots and c) are gain factors normalized to Pt/C specific activity at 0.9 V

Fig. 3. MOR polarization curves in 0.1 M HClO4 and 1 M methanol at rotation of 1600 RPM with 50 mV/s of Pt/C and two PtCu/C catalysts (black is platinum, blue is disordered and red is ordered), b) are Tafel plots and c) are gain factors normalized to Pt/C specific activity at 0.9 V
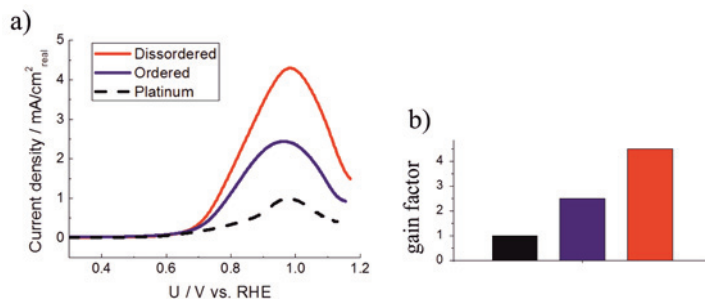
4. Discussion

From the vast knowledge already obtained on Pt alloyed catalysts one can learn that the increase of intrinsic activity is probably a consequence of changed adsorption properties of platinum surface atoms [7]. The more active Pt surface possesses decreased affinity for adsorption of oxygen species (like OH_{ad}) therefore yielding more free active sites for the ORR to take place. The origin of the enhanced activity lies in the addition of second metal which gives rise to intermetallic charge transfer and changes in the interatomic distances of the surface atoms (electronic or ligand and strain or geometric effect). This concept was first shown by Adzic on "Pt-monolayer" catalysts [2, 3, 4] followed by Stamenkovic and Markovic to explain the enhanced activity of "Pt-skin" catalysts [5, 6, 7]. A strong theoretical basis was provided by Nørskov with the DFT models of such systems [8, 9]. Strasser also has demonstrated enhanced ORR activity for the PtCu/C catalysts with the same alloying components as we have used later in the synthesis of our PtCu/C catalyst. His interpretation of enhanced activity is based on similar concept of lower OH_{ad} coverage as a consequence of the strain effect [10]. Therefore, we can safely conclude from our superior ORR specific activities that the ordered PtCu/C surface possesses a decreased affinity to adsorbed hydroxyl species (OH_{ad}) with respect to disordered and Pt/C standard.

This might also be the reason why at the same potential (0.9 V) more methanol oxidizes on the ordered PtCu/C catalyst surface than on the others (Figure 3b). Since the transfer of the first electron is the rate determining step [11], the same as for ORR [1], it is then also likely influenced by the coverage of the adsorbed oxygen species (like OH_{ad}). Whereas at low potentials (0.6 V) the onset of MOR is highly dependent on the ability of the surface to remove the stable poisoning intermediates (especially CO) [11]. Here the bifunctional mechanism is the decisive step and the presence of Ru on the surface that is known to activate water at lower potentials than Pt to form reactive partner (OH_{ad}) for CO removal, is welcome [12]. However, at higher potentials CO is not stable anymore and therefore it does not act as a poison. A similar conclusion can be made as in the case of ORR where the more active surface is the surface that is less occupied by the oxygenated species; in our case this is the ordered catalyst.

Additional ordering or intermetallic compounds in the Pt based catalysts is a phenomenon that has already been described in the literature [17]. It has been shown on the example of $PtTi_3$ catalyst that ordered phase shows slightly higher catalytic activity for formic acid oxidation and MOR [18] however the particle size was not the same (ordered 37 ± 23 nm, disordered 3 ± 0.4 nm). The same authors also showed enhanced activities for PtPb [19] as did others [20], but there have been no measurements of the disordered phase activity. The absence of systematic comparison between ordered and disordered phases in the literature contributes to the lack of definitive answers if and why the ordered phase is more (or less)

active than the disordered one. Researchers from General Motors have shown the enhanced activity of PtCu/C. Although they did observe a low degree of ordering [22], they could not directly correlate it to the enhanced ORR activity. An interesting work has been done on PtCo/C catalysts where three catalysts with the same Pt:Co (1:1) ratio but with different amounts of multiple phases were compared [21]. An increase in ORR activity for the "disordered" catalyst was observed. Since in our study the ordered and the disordered catalysts are made from the same precursor (first the ordered catalyst was annealed and than a part of it was again heated and quenched to obtain the disordered one), both catalysts have the same atomic ratio of Pt and Cu and the same particle size distribution. The only obvious systematic dissimilarity (difference) is in the XRD spectra, where the ordering is recognized by additional diffraction peaks (Figure 1a). This led us to the conclusion that the activity enhancement is directly correlated with the presence or ordered phase. The question why the ordered phase is more active than the disordered one is however still not resolved and it is a focus of our further research.

Specific activity of the catalyst is just one of the parameters that are influencing the efficiency of a fuel cell. To obtain high mass activity, which is the product of a specific activity and electrochemically active surface area (ESA or ECA), we have to increase one or the other factor or both of them. One of the obvious ways to raise ESA is to make the particles smaller. However the problem of smaller particles is that their specific activity drops (due to the well known particle size effect) [1]. While we raise ESA we lower the specific activity, therefore mass activity receives practically no gain. Another way is to make a core shell catalysts that already have much higher ESA at the same particle size. Spherical particles in size of 10 nm the core shell with Pt:Cu atomic ration of 1:3 have four times bigger ESA than pure platinum sphere particle of similar size (figure 4). In a monolayer type catalyst, the ESA of 10 nm particle is ca. six times higher and is actually particle size independent (constant) [2, 3, 4, 23]. When all the Pt atoms are on the surface of all the particles then the theoretical ESA is 152 m^2/gPt (red curve in figure 4). This leeds to the important conclusion that the ESA and particle size are not directly correlated and should not be used as the same parameter. As regards the mass activity ESA is the decisive parameter and not particle size! In order to enhance mass activity we must increase the specific activity or ESA.
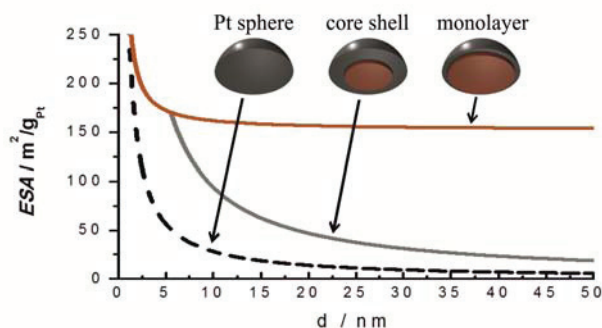

Fig. 4. A calculation of *ESA* as a function of a particle diameter for pure Pt sphere, Pt@Cu core shell and Pt monolayer on Cu sphere.

5. Conclusion

The increase of specific activity of proprietary PtCu/C-based catalyst in ORR and MOR is induced by partial ordering of the crystal structure (Pm-3m). These catalysts are by a factor of two more active than the ones containing only disordered (Fm-3m) phase. The concept of the monolayer type catalyst which activity is particle size independent was explained.

Acknowledgements

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