



Interrelation between catalytic activity for oxygen electroreduction and structure of supported platinum



Alexandr G. Oshchepkov^{a,b}, Alexandr N. Simonov^{c,*}, Pavel A. Simonov^{a,b}, Alexander N. Shmakov^{a,b}, Nina A. Rudina^a, Arkady V. Ishchenko^a, Olga V. Cherstiouk^{a,b}, Valentin N. Parmon^{a,b}

^a Borekov Institute of Catalysis, Novosibirsk 630090, Russia

^b Novosibirsk State University, Novosibirsk 630090, Russia

^c School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

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ABSTRACT

Electrocatalytic activity for the oxygen reduction reaction (ORR) of the carbon-supported Pt catalysts obtained by chemical and electrochemical deposition has been studied in 0.10 M HClO₄ at 293 K in the expectation to gain new insights into the influence of the substructure of platinum on its catalytic properties for the ORR. Electron microscopy, XRD and electrochemical techniques have been employed to demonstrate that: (i) the ‘chemically’ synthesised Pt/C catalysts contain highly-dispersed isolated metal particles at intermediate metal loadings and both isolated crystallites and crystallite aggregates at higher loading; (ii) the electrodeposited Pt/C materials are ‘nanostructured’, *i.e.* contain large (up to *ca* 350 nm) aggregates with the deposition potential dependent morphology composed of comparatively small (<20 nm) platinum crystallites. No structural dependence of the ORR catalytic properties for the ‘chemically’ synthesised Pt/C catalysts has been revealed, except for the well-known negative size effect. On the contrary, platinum electrodeposited on glassy carbon or furnace black demonstrates atypically high ORR catalytic activity, especially, when electrodeposition is undertaken at 0.10 V. Presumably, easily oxidisable defect sites, intergrain boundaries in particular, present at comparatively high concentrations in the electrodeposited materials provide efficient adsorption of O₂, which further reduction occurs at the highly catalytically active Pt(111) facets. Structural defects present at an optimal concentration are concluded to promote the ORR catalytic activity of platinum, but excessive defectiveness of the Pt catalyst might hinder the kinetics of the oxygen electroreduction.

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1. Introduction

Improvement of the efficiency of heterogeneous (electro)catalytic materials is usually achieved *via* careful selection of composition of the active component of a catalyst, which nowadays is often underpinned by theoretical predictions available owing to remarkable progress in the development of theoretical calculation methods [1,2]. For supported catalysts, performance also can be improved by choosing a support with optimal textural characteristics [3]. Another important parameter that can be crucial in determining the adsorption and catalytic properties of the material is its structure, *viz.* size, surface crystallography and defectiveness of particles as well as their mutual alignment.

Significant investigative efforts towards understanding the relation between the structure and the electrocatalytic properties of metal electrodes have been made. On the basis of the studies performed with single crystal electrodes and supported nanoparticles, structure sensitivity of a variety of the adsorption and electrocatalytic processes has been revealed [4]. Those include both fundamentally and practically relevant CO adsorption/oxidation [5–7], methanol oxidation [8], hydrogen oxidation/evolution reactions [5,6,9] and oxygen reduction reaction (ORR) [10] on metal electrodes.

The structure sensitivity of the Pt-catalysed ORR in the acidic medium has been subject to significant number of studies, predominantly, on the perspective of elaboration of an efficient cathode catalyst for the proton exchange membrane fuel cells. The negative size effect for the platinum electrocatalysts of the ORR, *i.e.* decrease of the surface-weighted specific activity of Pt particles with the decrease in their size, is proven to arise from the enhancement of propensity of the Pt surface to oxidation upon increasing

* Corresponding author. Tel.: +61 3 9905 1520.

E-mail addresses: alexandr.simonov@monash.edu, sanfc@gmail.com (A.N. Simonov).

the metal dispersion [11–15]. Enhanced energy of adsorption of the oxygen-containing species and, consequently, higher surface coverage with the inhibiting OH_{ads} species on small Pt nanoparticles makes their surface-weighted specific ORR activity lower as opposed to that of coarse platinum catalysts at the same potential. Low-index Pt crystal faces also notably differ in the adsorption energies of the oxygen-containing species [6,16]. Namely, the Pt(100) plane demonstrates higher affinity to OH_{ads} and O_{ads} as compared to Pt(111), while Pt(110) is the most preferred for the OH_{ads} and O_2 adsorption [6,16–20]. Accordingly, Pt(111) excels Pt(100) in terms of the intrinsic ORR activity in the absence of adsorbing species different from OH_{ads} ,¹ as it has been demonstrated, e.g. by Marković et al. [6,17] when using either KOH or virtually non-adsorbing HClO_4 as the supporting electrolyte. Although Pt(110) demonstrates the highest affinity to OH_{ads} , its ORR activity is either close to or slightly lower than that of Pt(111) [18,19]. However, the difference in the ORR activities of the most active Pt(111) and the least active Pt(100) crystal faces does not exceed a factor of ten [6,17–19].

Nevertheless, the postulated differences in the adsorption and catalytic properties of the Pt crystal faces can be harnessed for creation of a better ORR catalyst exploiting a ‘division of labour’ philosophy as demonstrated by You et al. [21]. In such a catalyst, easily oxidisable Pt(100) is assumed to provide fast adsorption of O_2 , which may further diffuse to the Pt(111) surface for efficient catalytic reduction on condition that the nanoscale proximity of the crystalline facets enabling fast diffusion of the adsorbed species is provided. In principle, an analogous strategy for improvement of the ORR catalytic activity of Pt might be employed by using structural defects, which are very reactive to the oxygen-containing species [22–26], as active sites for the O_2 adsorption. In this case, the nanoscale proximity between the highly catalytically active Pt(111) and efficient O_2 adsorption sites should be provided *a priori*. Indeed, Feliu et al. [25] reported slightly enhanced ORR activity of the stepped Pt surfaces as compared to that of Pt(111). On the contrary, You et al. [26] and Shao-Horn et al. [27] found no or even deteriorating effect of the steps on the ORR activity of Pt. At the same time, You et al. [26] hypothesised that the steps positively affect the ORR activity of Pt only if the ratio between the Pt(100) and Pt(111) facets is optimal. However, if Pt(100) is predominant on the (111)–(100) nanofaceted surface, its ORR activity will be lower than that of Pt(111). Recently, a promoting effect of the intergrain boundaries (IGB) on the ORR catalytic activity of Pt has been proposed [28], but the reported data on the oxygen reduction current densities (j_{ORR}) for both “defect rich” and “defect poor” catalysts are contradictory (*cf.* j_{ORR} reported in the main text and Supporting Information of Ref. [28]). Thus, it can be concluded that an ambiguity in the influence of the defects on the catalytic properties of platinum for the ORR still remains. At the same time, a well-defined positive influence of defects and the IGBs has been established for several catalytic [29,30] and electrocatalytic processes [1,6,31–37].

In this paper, we report and attempt rationalisation of the ORR activities of a set of the supported ‘nanostructured’ (*i.e.* consisting of a multitude of nm-sized crystallites connected via the IGBs) platinum deposits differing in morphology and defectiveness with the aim to further advance in understanding of the relation between the substructure of Pt catalysts and their activity for the O_2 electroreduction. Fabrication of the defective ‘nanostructured’ materials has been performed by *electrodeposition* method. Importantly, this synthetic strategy allows tuning the structural properties of electrodeposited Pt by variation of the deposition potential (E_D)

[37,38]. The ORR catalytic properties of the isolated Pt crystallites and Pt crystallite aggregates *chemically* deposited on a high-surface area carbon are reported for comparison.

2. Experimental

2.1. Materials

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (98%), HCl (36%, Sigma Tec), HNO_3 (70%, Reachim), Na_2CO_3 (99%, Reachim), NaOCH (99.0%, Reachim), HClO_4 (60%, Fluka), H_2SO_4 (96%, Acros) were used as received. Commercial furnace black Vulcan XC-72 (hereinafter, XC72) (Cabot; specific BET area, $A_{\text{BET}} = 222 \text{ m}^2 \text{ g}^{-1}$, micropore volume, $V_{\mu} = 0.026 \text{ cm}^3 \text{ g}^{-1}$) and mesoporous graphite-like carbon material Sibunit (Sib.1562) (Institute of Hydrocarbons Processing, Russia; $A_{\text{BET}} = 449 \text{ m}^2 \text{ g}^{-1}$, $V_{\mu} < 0.001 \text{ cm}^3 \text{ g}^{-1}$) obtained via hydrocarbon pyrolysis and subsequent activation [39] were employed as catalyst supports. Supported 20, 40 and 60 wt.% Pt/Sib.1562 catalysts were synthesised as described elsewhere [3,40]. For the catalyst preparation and electrochemical measurements, high-purity gases (Ar 99.998%; O_2 99.99%; CO 99.999%; H_2 99.99%) were used. All solutions were prepared using Milli-Q (Millipore) purified water (18.2 M Ω cm).

2.2. Electrochemical procedures

Electrochemical measurements were undertaken in a jacketed three-electrode cell thermostated at 298 or 293 K using an Autolab PGSTAT 30 potentiostat (EcoChemie) equipped with a Scangen module. The counter electrode (high surface area Pt foil) and the reference electrode ($\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4(\text{sat.})$) compartments were connected with the working electrode chamber via a glass frit and a Luggin capillary, respectively. All electrode potentials reported in this paper are referred to the reversible hydrogen electrode (RHE).

A glassy carbon (GC) cylinder (5 mm diameter), which flat top surface was modified with a tested catalytic material (Pt/Sib.1562 or electrodeposited Pt), or a polycrystalline Pt foil, or a Pt disk (EcoChemie; diameter 3 mm) were employed as the working electrodes. Standard procedures used for pretreatment of the GC substrates and Pt electrodes and method used for immobilisation of the Pt/Sib.1562 catalysts on the GC surface are detailed in [Supporting Information](#).

Electrodeposition of Pt was performed at 298 K in a potentiostatic regime at the deposition potentials $E_D = 0.05, 0.10, 0.20, 0.30$ or 0.40 V vs. RHE from the deaerated $0.01 \text{ M H}_2\text{PtCl}_6 + 0.01 \text{ M HCl}$ solution as described by Plyasova et al. [38]. Pt was electrodeposited either directly on a GC surface, or on a thin layer of XC72 (8 μg) predeposited on GC using the same procedure as for immobilisation of Pt/Sib.1562. Faradaic efficiency of the employed electrodeposition procedure was not worse than 98% (see [Supporting Information](#)). After deposition, the samples were polarised at 0.10 V vs. RHE in $0.10 \text{ M H}_2\text{SO}_4$ for 3 min to desorb chlorides. Further characterisation of the electrodes was undertaken in 0.10 M HClO_4 .

For CO-stripping experiments (voltammetric oxidation of CO monolayer pre-adsorbed on Pt), CO was adsorbed at 0.10 V vs. RHE for 5 min at 298 K in 0.10 M HClO_4 and then removed from the electrolyte by Ar purging for 45 min keeping the electrode potential fixed at 0.10 V vs. RHE .

The ORR catalytic activity was derived from the rotating disk electrode (RDE) voltammetric data (scan rate, $v = 0.02 \text{ V s}^{-1}$) obtained in O_2 -saturated 0.10 M HClO_4 using an Autolab RDE-2 setup at the rotation rates (ω) of 400, 900, 1600 and 2500 rpm. Electrochemically active surface area of platinum for the

¹ Unless otherwise stated, the ORR activity of platinum determined in the absence of interfering adsorbing species like (bi)sulfate is discussed below.

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