Research paper

Loading effect of carbon-supported platinum nanocubes on oxygen electroreduction

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ABSTRACT

In this work, Vulcan carbon-supported cube-shape Pt nanoparticles with various metal loadings were synthesised in the presence of oleylamine and oleic acid. Surface morphology of different Pt/C samples was examined by transmission electron microscopy (TEM) and their metal loading verified by thermogravimetric analysis (TGA). TEM micrographs showed Pt nanoparticles with a preferential cubic-shape and increased agglomeration of the particles with increasing Pt loading. Electrochemical characterisation of the Pt/C catalysts indicated that the resulting Pt nanoparticles present a preferential (100) surface structure. The electrocatalytic properties of the Pt/C catalysts of different metal loading were evaluated towards the oxygen reduction reaction (ORR) both in acidic and alkaline media employing the rotating disk electrode (RDE) configuration. Interestingly, similar specific and mass activities were found in both solutions revealing that the ORR activities were independent of the Pt loading and suggesting that all the Pt nanocubes contributed as isolated particles.

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1. Introduction

Recent decades of research have shown that low-temperature fuel cells are promising and sustainable environmental-friendly power sources in the future [1–3]. Platinum-based catalysts show the highest electrocatalytic activity towards the oxygen reduction reaction (ORR) on the cathode of the low-temperature fuel cells [1,3,4]. Although platinum (Pt) is the best cathode catalyst for fuel cells [5,6], it is still important to decrease the amount of this expensive and scarce noble metal in the platinum-based catalysts [4,5]. On the other hand, particle size and catalyst surface structure are thought to be directly related to the electrocatalytic activity of Pt for ORR [7,8]. In this regard, the control of the shape and composition is highly favourable to create new Pt-based nano-structures and to utilise scarce Pt more efficiently [9].

It has been established that the electroreduction of oxygen on single-crystal Pt surfaces is a structure-sensitive reaction [10]. The O_2 reduction studies on Pt(hkl) electrodes in aqueous 0.1 M $HClO_4$

and 0.1 M KOH solutions by Markovic et al. revealed that in alkaline media the ORR activity decreases in the following sequence $(111) > (110) > (100)$, while in perchloric acid the variation in the O_2 reduction activities was found to be rather small between the three low-index facets, with activity increasing in the order $(100) < (110) \approx (111)$ [11–13]. Moreover, the order of the ORR activity on Pt (hkl) in sulphuric acid is completely different and decreases as follows: $(110) > (100) > (111)$ [14]. It has been proposed that the differences in the activity in H_2SO_4 arise from stronger adsorption of the (bi)sulphate anions, which are considered as spectator species inhibiting the ORR process. On the stepped Pt surfaces it was found that the ORR activity in sulphuric and perchloric acid on Pt(111) was the lowest [15]. The O_2 reduction activity of Pt(110)-(1×1) was found to be lower than that of disordered Pt(110)-(1×2) in 0.1 M $HClO_4$ by 30–40 mV on the basis of the half-wave potential value [16].

The structure-sensitivity of the ORR process on Pt(hkl) low-index facets should lead to particle size effects according to the Kinoshita's cubo-octahedral model of Pt particles [17]. Several efforts have been made to understand the Pt particle size effect on the ORR kinetics [6,18–28]. Mayrhofer et al. have reported in their early studies that the specific activity (SA) for O_2 reduction increases when the particle size increases [20,21]. This activity
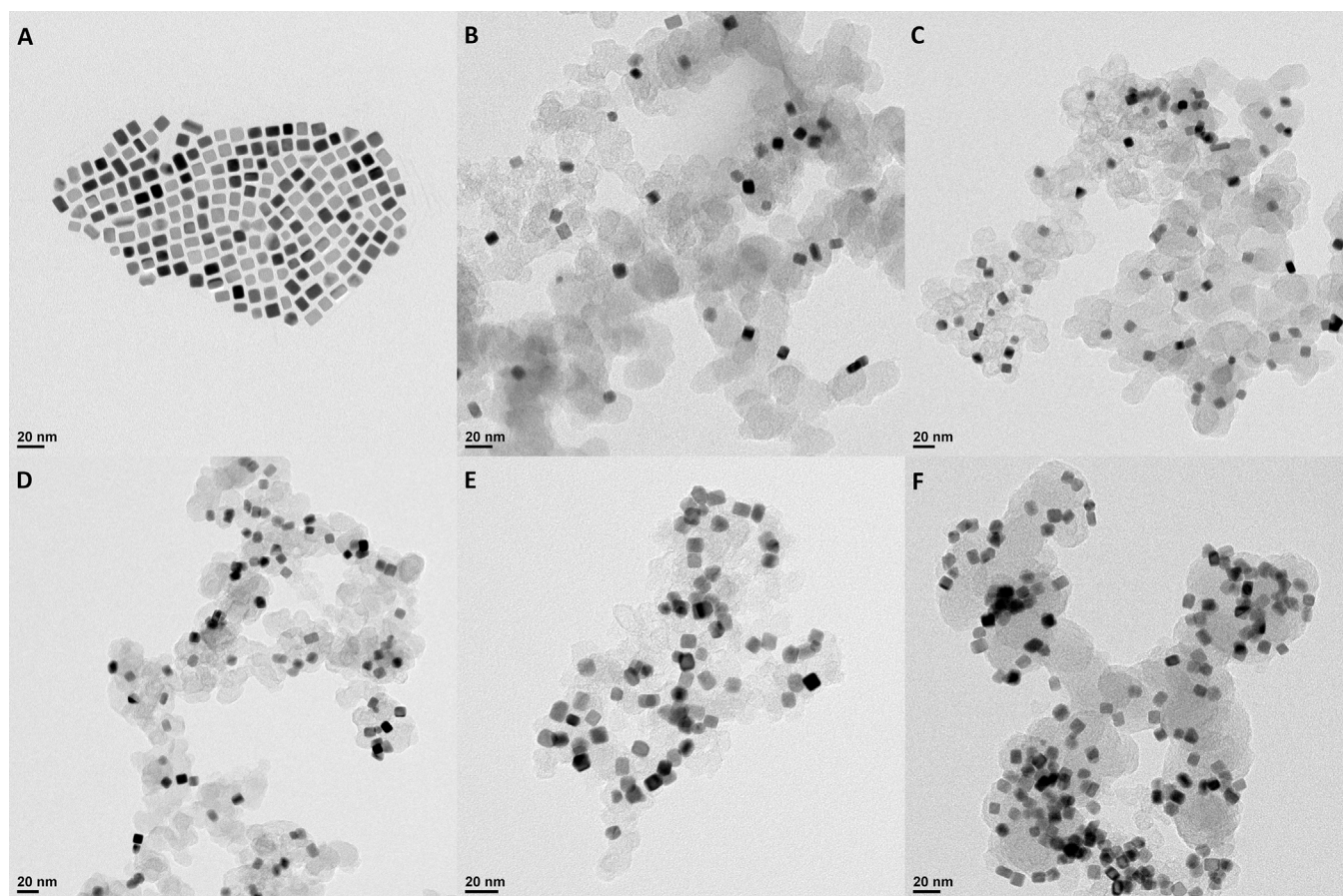
Fig. 1. TEM micrographs of (a) unsupported Pt nanocubes, and carbon-supported cubic Pt nanoparticles: (b) 10, (c) 20, (d) 30, (e) 40 and (f) 50 wt% Pt/C catalysts.

change could be related to the higher Pt surface coverage by oxygen-containing species, which strongly block the active sites with decreasing Pt particle size. Sheng et al. studied the size-dependence of the ORR activity of Pt particles (size below 5 nm) on high-area carbon support in acidic electrolytes [22]. However, their results did not express any influence of the size on the specific and mass activities (MA) for O_2 reduction. Whilst the work by Sheng et al. revealed that the O_2 reduction activity was independent of the Pt particle size, it has been reported by Shao and co-workers that both SA and MA depend on the Pt particle size, if the particle diameter is under 10 nm [23]. These authors suggested that this behaviour is related to the oxygen binding energies on different Pt sites, which get accessible when the particle size changes. Furthermore, Shinozaki et al. [27], who varied the Pt particle diameter from 2 to 10 nm, showed that in 0.1 M $HClO_4$ solution the SA increased from 0.8 to 1.8 mA cm^{-2} with increasing particle size, and for particles bigger than 10 nm the activity plateaued to 2.7 mA cm^{-2} at 0.9 V vs RHE. It has been suggested by Mukerjee and McBreen that the decrease in the ORR electrocatalytic activity on smaller Pt particles (size below 5 nm) is related to the increase of Pt low-coordination sites on the surface of platinum nanoparticles, which inhibits the electroreduction of O_2 due to the strong adsorption of OH above 0.8 V vs RHE [19].

Conversely, several workgroups have studied Pt loading effect on the electrocatalytic activity for oxygen reduction [29–35]. Shih et al. varied the amount of the catalyst on the electrode surface [29], finding out that the SA was independent of the Pt loading on a carbon black support and it was considered to represent the intrinsic ORR activity of the catalyst. Quite similar results have

been also reported by Higuchi et al., who changed the Pt loading level on carbon black from 19.2 to 63.2 wt% and found that the SA was almost constant for all the catalysts studied [30]. Keeley and co-workers showed that by employing low and ultra-low Pt loadings in fuel cells, the electrocatalytic activity did not depend on the amount of material used, however the stability diminished remarkably [31]. On the other hand, it was found by Schmidt and co-workers that by increasing the loading of Pt on the carbon support the SA for O_2 reduction increased, but MA decreased [32,33]. These changes were caused by the transition from the state of isolated Pt nanoparticles to larger agglomerates. Strong correlation between the metal loading and the ORR activity was also shown by Speder et al. [34], when the Pt loading increased from 20 to 80 wt%, the SA increased from 470 to 775 μA cm^{-2} and MA values raised from 350 to 625 A g^{-1} in 0.1 M $HClO_4$ solution at 0.9 V vs RHE.

The uniform distribution of the catalyst on top of the glassy carbon (GC) electrode plays a critical role in the electroreduction of oxygen. Some research groups have aimed to prepare uniform catalyst coatings and understand the effect of even distribution on the reproducibility [36,37]. Ke et al. used an in-house-developed automated electrode preparation device, which transferred ~3 nL droplets of the sonicated suspension of the Pt/C catalysts to controlled positions on the GC substrate [36]. This coating procedure resulted in higher diffusion-limited current values than inhomogeneous layers and these values were comparable to the theoretically calculated one. Also the reproducibility was much higher with the uniformly distributed catalyst layer. Another approach, which has been also used in the present research, was