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Formation of Pt/Pb nanoparticles by electrodeposition and redox replacement cycles on fluorine doped tin oxide glass

Kirsi Yliniemi[a,b,*,1], David Wragg[b], Benjamin P. Wilson[a,1], H. Neil McMurray[b,1], David A. Worsley[b,1], Patrik Schmuki[c,1], Kyösti Kontturi[a,1]

[a] Aalto University, Department of Chemistry, P.O. Box 16100, 00076 AALTO, Finland
[b] SPECIFIC, Swansea University, Baglan Bay Innovation & Knowledge Centre, Unit 20 Central Avenue, Baglan Energy Park, Baglan, Port Talbot SA12 7AX, United Kingdom
[c] Department of Materials Science, University of Erlangen-Nuremberg, WW4-LKO, Martensstrasse 7, 91058 Erlangen, Germany

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ABSTRACT

A two-stage approach that combines electrodeposition with redox replacement has been used to deposit Pt/Pb nanoparticles on fluorine doped tin oxide (FTO) glass. The deposition takes place by cycling between the two steps in a single electrolyte bath containing both Pb^{2+} and Pt^{2+} ions. In the first step, Pb is electrodeposited on FTO glass at a potential E_1 and in the second step, Pt replaces the sacrificial Pb directly on the surface at open circuit conditions until the open circuit potential reaches a value E_2. This method allows a quick deposition of Pt/Pb nanoparticles on FTO glass and the effects of E_1 and E_2 on the Pt/Pb formation and nanoparticle coverage of the surface were studied with SEM and XPS.

1. Introduction

Electrocatalysis using Pt is an attractive option for a large range of applications (fuel cells, automotive industry, petrol industry, etc.) due to its high catalytic activity and stability [1]. Currently, Pt is the most common candidate for the redox catalyst in dye-sensitized solar cells, an application which has seen much development during the last few decades since its introduction by Grätzel and co-author [2]. Due to the high costs of bulk Pt (and other Pt group metals), the use of nanoparticles has been subject to a lot of interest as they can enhance performance, mainly by multiplying the surface area by several factors, but also due to possibility of using different surface structures of Pt [1]. Therefore, the formation of Pt nanoparticles (PtNP) has seen intensive research with common methods including chemical reduction of platinum salts [3–6], electrodeposition [7–10] or sputtering [11,12].

Electrodeposition of PtNPs offers a quick and versatile route for nanoparticle formation as the deposition is readily controllable by potential or current [7]. In solar cell technologies, the demand for a transparent substrate material has been met by using fluorine doped tin oxide glass (FTO). However, FTO has a far less defined surface topography than, for example, Au(1 1 1) – which is often used for electrodeposition studies – and therefore the deposition process becomes less straightforward. Moreover, the semiconductive nature of FTO complicates the electrodeposition process when compared to the metal surfaces [8]. A range of studies have conducted different types of electrodepositions of Pt on FTO glass to be used as counter electrodes in DSSC applications [9,10,13–16]: for example, Li et al. [13] showed improved DSSC performance when the counter electrode consisted of electrodeposited, pre-prepared Pt nanoparticles on FTO glass compared to electroplated Pt/FTO electrodes and Kim et al. [9], on the other hand, studied both direct and pulsed current electrodeposition of Pt. According to them [9], a direct current electrodeposition yielded a dendritic growth of Pt while a pulsed electrodeposition resulted in much higher surface area of Pt nanoparticles on FTO and a better performance of DSSC. Ko and Kwon [8] have studied the nucleation mechanism itself and they found that overpotential can be used to tune the Pt nanoparticle size and density on the FTO surface: when the overpotential is high enough (i.e. applied cathodic potential), all the nucleation sites are activated and in general, the particle density increases but simultaneously, the particle size decreases due to the overlapping of diffusion layers around nucleation points [8].

An interesting approach for Pt thin film deposition called surface-limited redox replacement (SLRR) has been introduced by Brankovic and co-authors [17,18]. The SLRR process takes place in two sequentially repeated steps. First, a sacrificial material is underpotential deposited (UPD) during a short potential step (1 s) and then, the more noble metal ions present in the (next) electrolyte bath selectively dissolve and replace the sacrificial material

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* Corresponding author at: Aalto University, Department of Chemistry, P.O. Box 16100, 00076 AALTO, Finland. Tel.: +358 50 592 3690; fax: +358 9 470 22580.
E-mail address: kirsi.yliniemi@aalto.fi (K. Yliniemi).

[1] ISE member.

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on the surface at open circuit conditions due to the difference in the redox potentials. Recently, Viyannalage et al. [19] introduced an SLRR method in which thin films can be formed by using a single electrolyte bath – as opposed to the original SLRR method. This study was followed by Fayette et al. [20] who investigated a method where both Pb^{2+} (sacrificial material) and Pt^{2+} ions are present in slightly acidic conditions in the same electrolyte bath: they have shown that homogenously distributed Pt cluster networks can be formed in this way on Au(1 1 1) surfaces.

SLRR method has been used solely for thin film depositions and mainly on well-structured metal surfaces (such as Au(1 1 1)) and only few groups have studied the redox replacement on other surfaces: for example, Mkwizu et al. [21] prepared multilayers of bimetallic Ru|Pt nanocluster on glassy carbon using redox replacement reactions.

The galvanic displacement (GD) alone – an alternative term for redox replacement step – on the other hand, has been utilised for preparing nanostructures on semiconductor surfaces, such as on Si or Ge [22] and InP(1 0 0) and GaAs(1 0 0) surfaces [23]. It has also been used in core–shell nanoparticle synthesis, where particles are mostly present in the liquid phase [24,25]. Moreover, the combination of electrodeposition and GD has been reported for preparation Ru/Ni [26] and Pt/Ni surfaces [27], nanoporous Pt/AuCu on Pt/Ti/Si electrodes [28], CoRuPt catalysts on carbon paper [29] or Pt shell–Cu core nanoparticles on carbon nanowalls [30], amongst others. An interesting method was introduced by Du et al. [31] who prepared Pt/Pd nanospheres on indium tin oxide glass using a three step process involving electrodeposition of polystyrene templated Pt spheres, underpotential deposition of copper and galvanic replacement of Cu with Pd. These studies are usually performed in separate electrolyte baths and without subsequent cycling between electrodeposition and GD steps. To the best of our knowledge, there are no reports of utilising SLRR type methods or repetitive electrodeposition/galvanic displacement cycles on a FTO surface.

The results presented in this paper introduce a quick deposition method for the formation of Pt/Pb nanoparticles on FTO glass. This method resembles SLRR method performed in a single electrolyte bath [20] but instead of aiming at homogenous thin film deposition via underpotential deposition on a well-structured metal surface, the goal is to form nanoparticles on the FTO surface by repetitive cycling of electrodeposition and redox replacement with Pt. The replacement of Pb by Pt and the surface coverage are investigated by SEM and XPS.

2. Experimental

Fluorine doped tin oxide (FTO-15, SnO_2:F) glass was purchased from Solaronix. Preparation involved cleaning by sonication; first in distilled water for 5 min, then in ethanol (p.a., Sigma–Aldrich) for 5 min and finally, drying with N_2.

The electrolyte solution consisted of 0.1 M $NaClO_4$ (>98%, ACS reagent, Sigma–Aldrich), 1 mM $Pb(ClO_4)_2 \cdot 3H_2O$ (98%, ACS reagent, Sigma–Aldrich), 0.5 mM $K_2[PtCl_4]$ (99.9%, Aldrich) and 10 mM $HClO_4$ (70%, analytical reagent grade, Fisher Scientific). The solution was purged for 2 h with N_2 prior to deposition and cyclic voltammetry measurements.

Modifying the SLRR procedure introduced previously by Fayette et al. [20] for Pt nanocluster networks on Au(1 1 1) surfaces, the Pt/Pb nanoparticle deposition was performed on FTO glass in a three-electrode cell: 1 cm^2 FTO glass (working electrode) was immersed in the electrolyte solution, Pt mesh (99.9% Goodfellow) was used as a counter electrode and an Ag/AgCl electrode was used as a reference electrode. All potentials in the text are quoted with respect to an Ag/AgCl reference electrode. The deposition was controlled using a potentiostat (Ivium Compactstat, Ivium Technologies) and the process consisted of two steps repeated immediately after each other until 10 full cycles were completed. In Step 1, Pb was electrodeposited using a reducing potential (E_1) for 1 s. It is likely that co-deposition of Pt takes place also during this step due to the higher reduction potential of Pt when compared to Pb, even if the concentration of Pb is twice that of Pt. However, the deposition of Pt is the desirable end result and as such, the co-deposition leads only to a higher Pt content in the nanoparticles. In Step 2, open circuit potential conditions were held during the redox replacement step until the predefined open circuit potential value (E_2) was reached or the maximum time (60 s) was achieved, whichever occurred first. A cut-off time of 60 s was introduced for Step 2 as in this way the samples are still comparable to each other and the replacement can be studied, instead of reaching ≈100% replacement of Pb to Pt. The samples were prepared using two different E_1 values (−0.75 V and −0.50 V) and E_2 values (0.20 V and 0.50 V): the samples were denoted as Samples 1–4 as introduced in Table 1.

Table 1
The sample labelling with the deposition potential (E_1) and the cut-off potential (E_2) for the replacement step.

Sample name	E_1 vs. (Ag/AgCl) (V)	E_2 vs. (Ag/AgCl) (V)
Sample 1	−0.75	0.20
Sample 2	−0.75	0.50
Sample 3	−0.50	0.20
Sample 4	−0.50	0.50

The E_1 and E_2 potential values were selected from cyclic voltammograms measured in the absence (0.1 M $NaClO_4$, 1 mM $Pb(ClO_4)_2$, and 10 mM $HClO_4$) and in the presence of Pt^{2+} ions (0.1 M $NaClO_4$, 1 mM $Pb(ClO_4)_2$, 0.5 mM $K_2[PtCl_4]$, and 10 mM $HClO_4$) in the same three-electrode configuration as used for the deposition at 25 mV/s.

The coverage of sample surfaces were further analysed by SEM (Hitachi S-4800, cold field emission gun; 10 kV). XPS (Physical Instruments 5600) was used to study the Pt/Pb ratios on the FTO surface when the E_1 (deposition potential) and E_2 (cut-off open circuit potential) were varied. For XPS measurements, Al Kα radiation (1486.6 eV, 300 W) was used for excitation and the XPS spectra of target elements were measured with the pass energy of 23.50 eV at 45° angle. Si wafer with a 100 nm top-layer of SiO_2 was used for thickness calibration and the atomic percentages were measured from an 800 μm^2 area at 1.3 nm (thickness) intervals (pass energy 117.40 eV). For atomic percentage determination, the peak areas were corrected with the sensitivity factors of the acquisition software (MultiPakV6.1A, Physical Electronics Inc., 1994–1999), namely the photoionization cross-sections of Scofield (σ) and the asymmetry parameter (β).

The XPS spectra were analysed using Origin 8.6 Pro software and Gaussian algorithm for the peak fitting. Local maximum was used to find visible peaks and the 2nd derivative to reveal the hidden peaks. Eight datapoints were manually selected for the baseline which was used for the peak finding: this baseline is shown with the XPS spectra for the each element.

3. Results and discussion

3.1. Determination of E_1 and E_2 by cyclic voltammetry

In order to determine the deposition potential (E_1), as well as an appropriate cut-off potential for redox replacement step (E_2), cyclic voltammograms were measured in the absence (Fig. 1a) and in the presence of Pt^{2+} ions (Fig. 1b).

Fig. 1a shows that the Pb deposition and stripping is a reversible process in the absence of platinum: the deposition takes place at −0.60 V and the stripping takes place at −0.45 V. However, clear differences are apparent when the cyclic voltammetry is