Electrochemistry Communications 62 (2016) 60–63

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Electrochemical formation of palladium nanoparticles in a salicylate-based hydrophilic ionic liquid: The effect of additives on particle morphology and electrochemical behavior

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ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form 23 November 2015
Accepted 1 December 2015
Available online 9 December 2015

Keywords:
Dendrimer
Electrolysis
Ionic liquid
Nanoparticle
Palladium
Surfactant

ABSTRACT

Palladium nanoparticles (PdNPs) were prepared via potentiostatic electrolysis using Pt gauze electrode in the room temperature ionic liquid 1-butyl-1-methylpyrrolidinium salicylate (RTIL BMP-SAL) containing $PdCl_2$ with/without additives of cationic surfactants and PAMAM dendrimer. PdNPs were directly formed and dispersed in the IL during the electrolysis, which was mixed with graphite powder (GP) to prepare the IL–PdNPs–GP composite electrode for the electrochemical oxidation of ethanol in alkaline solutions. Introducing additives into the IL significantly affected the morphology and electrochemical behavior of the PdNPs. A facile approach of metal nanoparticle preparation can be developed based on this study.

1. Introduction

Ionic liquids (ILs) are recognized solvents with unique physicochemical properties such as negligible vapor pressure and comprehensive non-bonding forces. They, therefore, have been utilized in various applications [1–3] including as the media for the metal nanoparticle (MNP) formation [4]. The high viscosity and the specifically adsorptive properties of ILs make them able to kinetically stabilize the MNPs. Stabilizing agents usually essential for preparing MNPs are not needed in ILs. Various untypical approaches were thus developed such as laser ablation [5], sputter deposition [6], radiation irradiation [7], and microwave-assisted formation [8]. Although these approaches are able to be a universal method for preparing various MNPs, they are not convenient to use, and sophisticated instruments are needed. Traditional chemical reduction was thus still used for preparing MNPs in ILs [9]. However, chemical reduction has limitations because of the finite strength of the reducing agents. Recently, Katayama et al. demonstrated that MNPs can be formed via electrolysis in ILs [10–12]. Theoretically, this approach can be developed to be a universal method for MNP preparation because the reducing strength was controlled by the applied potential but limited by the electrochemical window of the electrolytes; ILs are thus very suitable electrolytes because of their wide electrochemical window.

Here Katayama's method was used to prepare PdNPs. However, a new water-soluble hydrophilic IL BMP-SAL was used, and an approach directly combining the merits of IL and MNPs in one step was developed to prepare the IL–PdNPs–GP electrode for electrocatalysis. Marked effects of additives on the morphology of the PdNPs and on their electrocatalytic performance towards ethanol oxidation were observed.

2. Experimental

RTIL BMP-SAL was prepared using the previous procedures [13,14]. Electrochemical experiments were performed inside a glove box using a Princeton Applied Research (PAR 263A) potentiostat/galvanostat or outside a glove box using a CH Instrument (CHI 621A) electrochemical analyzer. Three-electrode electrochemical cell was used where the reference electrode was a $Ag/AgCl_{IL}$ [14] for IL electrolytes but a Ag/AgCl (NaCl saturated) for aqueous electrolytes. Pt wire was used as counter electrode, and separated from the bulk IL using a glass tube with porous tip.

PdNPs were formed by electrolysis at −1.4 V (vs. $Ag/AgCl_{IL}$) using Pt gauze electrode in BMP-SAL containing 50 mM $PdCl_2$ at 70 °C with/without hexadecyltrimethylammonium chloride (CTAC), hexyltrimethylammonium bromide (HeTAB), or third generation (G3) PAMAM

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http://dx.doi.org/10.1016/j.elecom.2015.12.001
1388-2481/

dendrimer. TEM and XRD were used to characterize the PdNPs. The ILs containing PdNPs were diluted using acetonitrile, and appropriate volumes of the dilute solutions were dropped on carbon-coated copper meshes for TEM observation. PdNPs dispersed in BMP-SAL with/without additives were mixed with fine GP to form IL–PdNPs–GP composite electrode using the published procedures [15]. The voltammetric behavior of ethanol was studied at the composite electrodes in 1 M NaOH.

3. Results and discussion

Salicylate anion (SAL^-) shows strong ligand properties, which can form complex ions with various transition metals, including $PdCl_2$ that is not particularly soluble in water or non-coordinating solvents. $PdCl_2$ is easily dissolved in SAL-based ILs such as the hydrophilic BMP-SAL to form Pd(II) species that can also be produced by anodization of Pd. The linear scan voltammogram (LSV) of a Pd wire electrode in this IL is shown in the inset of Fig. 1a. The arrow indicates the initial direction of potential scan. Two oxidative waves, a_1 and a_2, were observed, and a_2 corresponds to the bulk oxidation of Pd. Although Pd(II) can be formed via anodization of Pd metal, $PdCl_2$ was used in the following experiments because of the consideration for convenience. Fig. 1a shows the cyclic voltammograms (CVs) recorded at Pt electrode in BMP-SAL with/without 50 mM $PdCl_2$. Wave c_1 associated with the reduction $Pd(II) + 2e^- \rightarrow Pd$, and waves a_1 and a_2 (the same waves in the inset) are due to the oxidation of Pd deposited at wave c_1. Two oxidative waves similar to a_1/a_2, the a_1'/a_2', were observed in neat BMP-SAL but they were not seen at GC electrode (Fig. 1b), indicating that a_1'/a_2' might not result from the oxidation of the products produced at the cathodic limit but the oxidation of Pt electrode. The inset of Fig. 1b shows that the LSVs display the significant dependence of the two oxidative waves on the initial potential. Our previous study indicates that the cathodic limit of SAL-based ILs associated with the reaction $SAL^- + e^- \rightarrow SAL^{2-\bullet}$ [14]. More $SAL^{2-\bullet}$ was produced at the electrode surface at a more negative initial potential used for the linear scan voltammetry. The $SAL^{2-\bullet}$ may exhibit a stronger ligand property to Pt, compared with SAL^-. Pt thus could be oxidized during the anodic scan in the neat BMP-SAL after sufficient $SAL^{2-\bullet}$ was accumulated at the electrode. To study the voltammetric behavior of Pd(II) in more detail, potential was reversed at the same switching potential for three different delay times, and the CVs are shown in Fig. 1c. Apparently, a_1 and a_2 waves related to the oxidation of Pd, especially for wave a_2. It increased with prolonging the delay time because wave a_2 associated with the bulk oxidation (see Fig. 1a inset) of Pd that was accumulated in more quantity when the potential was stayed at wave c_1 longer. Two oxidative waves of Pd have been reported in basic BF_4-based and chloroaluminate ILs [16–18].

Potentiostatic electrolysis was performed using Pt gauze electrode in BMP-SAL containing $PdCl_2$ with/without additives at −1.4 V. The solutions gradually turned to brown and dark, indicating the formation of PdNPs. Several previous studies have indicated why MNPs can be formed by electrolysis and stably dispersed in IL [10,19]. Generally, the applied voltage-dependent adsorption of BMP^+ on electrode surface [20,21] leads to the formation of nano-sized grains of electrodeposits. Nano-scale electrodeposits are even dispersed into IL to be MNPs rather than adhered on electrode surface while thick BMP^+ layer is formed at a sufficiently negative potential [10]. Cations and anions of IL can adsorb on MNP surface to hinder the aggregation of particles. The corresponding TEM images of PdNPs are shown in Fig. 2. PdNPs were indeed formed in the IL by bulk electrolysis, indicating that potentiostatic electrolysis is a feasible and easy approach for the preparation of PdNPs in IL. Fig. 2 indicates that additives introduced certain effects on the morphologies of PdNPs. Generally, bigger PdNPs were produced from the ILs containing additives (Fig. 2c–e), compared with those produced from neat IL (Fig. 2a). This phenomenon implied that the additives may be able to adsorb on the nanoparticles to affect their formation and growth.

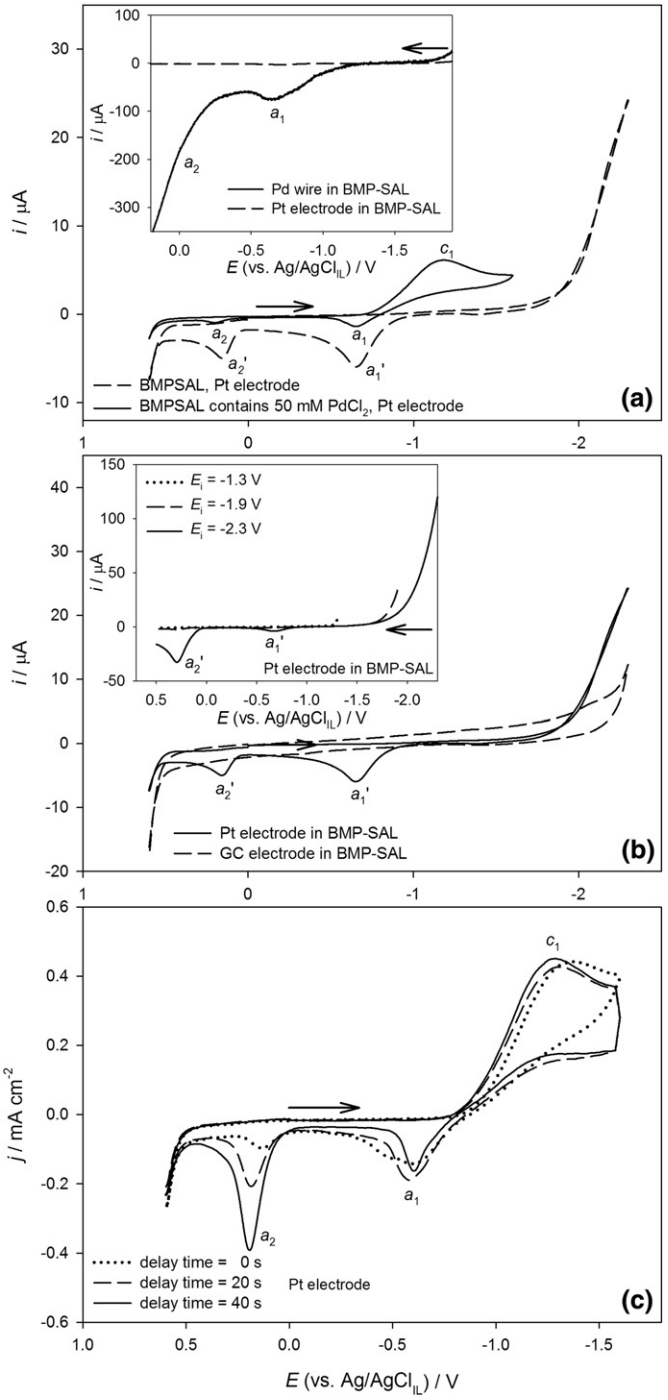

Fig. 1. CVs and LSVs recorded on the indicated electrodes in BMP-SAL with/without 50 mM $PdCl_2$ at 70 °C. Scan rate: 50 mV s^{-1}.

Except the PdNPs produced from the IL containing HeTAB, they were not individually dispersed but aggregated together to form scattered villages. If HeTAB is added, relatively more uniform and well-dispersed PdNPs could be obtained (Fig. 2d). The PdNPs, however, seemed to exhibit more diverse size, and significantly aggregate if PAMAM dendrimer is introduced. The different morphology of the PdNPs reflected on their electrochemical behavior towards the ethanol oxidation in alkaline solutions, and the corresponding observations are discussed later. Fig. 2b shows that PdNPs were dispersedly adhered on graphite after the PdNPs-containing IL was mixed with graphite powder to form the IL–PdNPs–GP composite via the previous method