Green synthesis and characterization of polyvinyl alcohol stabilized palladium nanoparticles: effect of solvent on diameter and catalytic activity

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Received 3 September 2016
Accepted for publication 20 March 2017
Published 5 May 2017

Abstract

Global palladium nanoparticles of different average diameters in the range 2–19 nm have been synthesized at room temperature by the reduction of K₂PdCl₄ in aqueous alcohols of varying composition in presence of constant proportion of polyvinyl alcohol (PVA). The synthesized nanoparticles have been characterized by different spectroscopic, microscopic and electro analytical techniques like cyclic voltammetry, chronopotentiometry, and chronoamperometry. FTIR spectroscopy detects the effect of co-solvent composition on the particle-PVA interaction involving –OH group of the latter. X-ray diffraction study shows that the nanoparticles have both face centred cubic and hexagonal crystalline structures which may influence the catalytic capability of the synthesized palladium quantum dots. The study reveals the influence of co-solvent (ethanol) composition in monitoring the average diameter and the nature of encapsulation of palladium nanoparticles which in turn help to monitor the electro-catalytic activity of the synthesized palladium nanoparticles in reference to oxidation of ethanol in alkaline medium.

Keywords: green synthesis, palladium nanoparticles, polyvinyl alcohol, solvent effect, ethanol oxidation, fuel cell

Classification numbers: 4.14, 5.00, 5.06

1. Introduction

Nanoparticles have attracted much attention in the last three decades because they show many novel properties different from bulk material. Because of high surface to volume ratio and property of confining electrons, these materials demonstrate unique mechanical, optical, electrical and magnetic properties [1]. Among all nanomaterials metal nanoparticles draw much attention due to their unique physical properties, chemical reactivity and potential application in various attractive fields like energy solution, communications, microelectronics, medical diagnostics, biocatalysts, sensors, fuel cells etc [2, 3]. Nanoparticles of many metals such as gold [4], silver [5, 6], platinum [6, 7], palladium [6, 8, 9], copper [10], ruthenium [6, 11] and rhodium [12] etc have been studied with a variety of experimental techniques.

Since palladium is a metal of platinum group, it is highly corrosion resistant and stable towards oxidation at the high temperature [6, 8]. Moreover it is relatively cheap so it has wide applications. It can serve as the hydrogen sensor, hydrogen storage materials [13, 14], and excellent electro catalyst in fuel cell [9, 15–18] low temperature reductant of automobile pollutants [19]. Palladium nanoparticles also found application in...
C–C coupling reactions [20, 21], biosensing [22], controlled drug delivery [23] and surface enhanced Ramon spectroscopy (SERS) [24]. It is also used in water de-nitrification [25]. Thus different synthetic protocols for palladium nanoparticles with small size and well defined morphology have become more and more interesting to meet the need of specific work. So, innovative synthetic methods have been developed to prepare palladium nanomaterials. Chen et al [26] studied seed mediated synthesis process to prepare uniform palladium nanorod with average length of about 200 nm and 300 nm and diameter of 20 nm through the addition of copper acetate solution. Glapell et al [27] reported the microwave synthesis and characterisation of palladium nanoparticle with average diameter of 4–5 nm and spherical shape supported on CeO₂, CuO, ZnO nanoparticle for CO oxidation. Cha et al [28] demonstrated the synthesis of morpholinum ionic liquid-stabilized palladium nanoparticles by electrochemical reduction. Liu et al [29] represented a methodology for synthesis of palladium nanospring structure using an anodic aluminium oxide (AAO) membrane template and facile electrochemical deposition. But they involve numerous types of reducing agents, mostly environmentally toxic and biologically hazardous. In order to minimize such hazards and wastage, green synthetic approaches attract much attention now a day’s [13, 30]. However, to date only a few numbers of reports have been found for preparation of palladium nanostructures done by a completely green synthetic approach.

Here we report green synthesis of palladium nanoparticles using aqueous mixtures of protic ethanol (EtOH) in presence of polyvinyl alcohol (PVA) which acts both as a reducing agent and steric stabilizer. PVA is known to protect the metal nanoparticles through the steric bulk of their frame work and the heteroatom play the role of the ligand, thereby stabilizing the nanoparticles [31]. Here it might be noted that ethanol possesses insignificant reducing capability at room temperature although it reduces Pd(H) to Pd(0) at ambient temperature [32]. Water is an ideal ‘green’ solvent due to environmental, economical and safety reasons [33]. Ethanol is a renewable, non-toxic protic solvent which can be easily obtained from chemical industry and fermentation of biomass [18]. More over pure solvents are extensively used for synthesis of nanoparticles of Pt metals [34]. These particles are well-behaved with respect to the electronic and optical properties [35]. So, it would be highly valuable to investigate the catalytic properties of the particles synthesized from these solvents. In addition, water is a versatile protic solvent widely used in the synthesis of colloids [36] and mixture of solvents sometimes play completely different roles from that of the pure solvents [37, 38]. Moreover, it was found in our previous studies [39] that the electro-catalytic capability of the polymer-protected nanoparticles of platinum metals is greatly dependent on the molecular environment near the surface of the synthesized nanoparticles. Such studies reveal that the presence of polymers prevents the approach of reactant molecules to the surface of synthesized nanoparticle constituting the electrode. So question arises whether such encapsulation of polymer can be controlled in order to improve the catalytic activity? The addition of an organic co-solvent which preferentially interacts with water may reduce encapsulation, which in turn may improve catalytic activity. So in this study, Pd nanoparticles are synthesized in different aquo-organic solvent mixtures with ethanol as co-solvents and the synthesized particles are characterized including their catalytic properties.

2. Experimental

2.1. Reagents and materials

Palladium chloride (PdCl₂) with a purity of 99% Pd approx from Arora Matthey Limited was purchased. KCl from Mark, India was used to prepare K₂PdCl₄ solution. PVA (number average molecular weight = 125000) from Lab Rasayan Co. was used as reducing and stabilising agent. The solvents used were of spectroscopic grade (spectrochem). All the other reagents were of AR/GR grade from Mark, India and used without further purification. Millipore water was used throughout.

2.2. Preparation of colloidal palladium nanoparticles

1 mass % of K₂PdCl₄ solution was prepared in a 25 ml volumetric flask using PdCl₂ (0.02271 g, 0.1281 mmol) and KCl (0.0191 g, 0.2562 mmol). PVA (0.5 g, 0.004 mmol) was also dissolved in 25 ml of hot water. Then five different sets of 1 mM solution of K₂PdCl₄, each containing 1 mass % of PVA were prepared in different aqueous ethanol mixed solvents containing 0, 10, 20, 30, 40 volume percent of ethanol by appropriate mixing of K₂PdCl₄ solution, PVA solution and pure ethanol.

The resulting palladium colloid may contain a minute quantity of unreacted PdCl₂ as impurity. To remove it, colloid purification was applied to the Pd/PVA system. The dispersed phase consisting of Pd/PVA nanoparticles was separated from the solvent medium with the removal of water soluble molecules or ions, excluding PVA, on treatment with excess butanol repeatedly. PVA did not dissolve in butanol. Nanoparticles trapped into the PVA matrix, collected by centrifugation, were re-dispersed in water with further formation of a Pd hydrosol. The unchanged nanostructure was confirmed by UV–visible spectroscopy of the sol.

2.3. Characterisation of the palladium nanoparticle

The ultraviolet–visible (UV–Vis) absorption spectra of the synthesized sol were obtained using a UV–Vis spectrophotometer (UV-1800 Shimadzu, Model TCC-240A) with quartz cells, between 250 nm and 800 nm. After certain time intervals, a small amount of Pd sol undergoing reaction was transferred to quartz cells of 1 cm path length, and spectrum was recorded against a water-solvent blank reference with base line subtracted. X-ray powder diffraction (XRD) studies were carried out using a (Bruker D8 Advance) diffractometer equipped with a Cu-Kα radiation source (λ = 1.5418 Å generated at 40kV and 40 mA). For this purpose each concentrated solution of palladium nanocrystallites was adsorbed on a small
amount of activated fine charcoal which was then dried by keeping it overnight inside vacuum desiccators. The shape and size of the particles were investigated using high resolution transmission electron microscope (TEM) (JEOL 2010 and operating at 200 kV). Samples for TEM were prepared by irradiating the diluted and cooled (for freeze the reaction at the time when the sol is taken) palladium sol with ultrasonic waves, using a sonicator (D-compact, SL no-1482) for about 45 min. A drop of the sol was cast on a 300 mesh carbon-coated copper grid, and the solvent was blotted off with filter paper after 10s of contact, followed by natural evaporation of the solvent at room temperature. The effect of PVA-solvent interaction was investigated using Fourier transform infrared (FTIR) spectroscopy. For the measurements, dry solid nano-composite were mixed thoroughly with a KBr pellet and analysed using a FTIR spectroscopy (Perkin Elmer, SN-74514).

The electrocatalytic behaviour of palladium nanoparticles obtained using different solvent was verified using cyclic voltammetric (CV), chrono potentiometric (CP) and chrono amperometric (CA) studies. For this, each Ni-supported electrode was prepared from the respective Pd hydrosol by chemical solution deposition using ‘drop and dry’ technique. Each electrode was covered with 20 µl 1% nafion solution. Electrodes are designated as Ni/Pd(1–5) for Pd nanoparticles synthesized from aqueous solvent containing 0%, 10%, 20%, 30%, 40% (v/v) ethanol. The CV, CP and CA of Ni-supported electrodes were studied in reference to the anodic oxidation of ethanol in alkaline medium using a computer-aided potentiostat/galvanostat instrument (Autolab Company). Electrochemical study was later executed in a two-component glass cell using a conventional three-electrode assembly. The reference electrode was Hg/HgO/OH° (1 M) (MMO), whose equilibrium electrode potential was ~0.1 V with respect to standard hydrogen electrode (SHE). In each measurement, a large Pt-foil (1 × 1 cm²) was used as a counter electrode and the potential data were recorded against those of MMO.

3. Results and discussion

3.1. UV spectroscopic analysis

On addition of K₃PdCl₄ to each solvent containing PVA at room temperature 25 °C ± 0.2 °C the colour immediately changes to light orange indicating the formation of Pd nanoparticles. The possible oxidation reaction of the reductant taking place with different solvent: (i) water and (ii) aqueous ethanol are given below. The O⁻² is the species which reacts with Pd²⁺ to convert it Pd(0). The formation of Pd nanoparticles with progress of time can be characterised by UV–Vis spectrophotometer.

Formation of Pd⁰ atoms by the main reductant PVA can occur according to the following equation:

\[
\begin{align*}
\text{H}_2\text{C} - \text{C} - \text{OH} & \quad + \quad \text{Pd}^{2+} \quad \text{OH} \\
\text{H}_2\text{C} - \text{C} - \text{O} & \quad + \quad \text{Pd}^0 + 2\text{H}^+ 
\end{align*}
\]

[6, 8]. With time the peak of Pd²⁺ ion started to disappear, suggesting reduction of the metal ions. The representative UV–Vis spectra of Pd nanoparticles in 40% ethanol recorded at different time intervals during the course of reaction are presented in figure 1(b). These profiles show increased absorbance at almost all wavelengths indicating additional absorbance of Pd(0) generated by reduction of Pd²⁺ ions. The absence of the peak around 420 nm for samples after 24h of reaction indicates the full reduction of Pd²⁺ to Pd(0). The time required for disappearance of peak is different for different solvent-mixture; suggest that the rate of formation of Pd(0) vary with varying the composition of binary solvent. Figure 1(c) represents the profiles for different solvents after disappearance of the peak.

In most cases, Pd metals do not show surface plasmon resonance (SPR) because it depends on several factors like molecular environment, solvent composition, temperature etc. For samples undergoing 6 min of the reaction, the wave length of SPR decreases on increasing the ethanol content in the binary solvent as evident from the inset of figure 1(a). This corresponds to the small increase in the diameter of Pd nanoparticles as evident from the subsequent TEM study. On allowing more time for the reaction, the said wavelength
decreases gradually for a given reaction medium, as represented by figure 1(b) for 40% ethanol, the wave length of SPR decreases even if particle grows during that time. This is because of the fact that fresh small particles are generated in the process, giving rise to smaller wavelength of SPR. When the samples are subjected to reaction of more than 3 h the SPR is invisible because it shifts to much shorter wave length than 300 nm.

3.2. X-ray diffraction (XRD) study

The formation of metallic particles in the graphite dust matrix was confirmed by XRD study. The curve (a) in figure 2 shows that three intense sharp peaks for Pd with 2\(\theta\) values 40.05°, 68.00°, 81.58° which can be assigned respectively, to the 111, 220, 311 planes of face centred cubic (fcc) lattice of palladium from JCPDS file no 88-2335. Other broad peaks at ca 43.69° is for body centred cubic or 100 of hexagonal graphite carbon or both. The average size of the metal nanoparticles were calculated from the full width at half maximum (FWHM) of three peaks using Debye-Scherrer equation. These are found to be 12 nm, 13 nm, 14 nm, 16 nm, 19 nm respectively for nanoparticles synthesized from 0%, 10%, 20%, 30%, 40% (v/v) ethanol water mixture, after 24 h completion of the reaction. Curve (b) in figure 2 depicts XRD pattern of Pd obtained from 10% ethanol solvent shows two peaks at 2\(\theta\) values of 67.88° and 81.22° which might be due to 220 and 311 planes of fcc or 110 and 113 planes of hexagonal Pd. Since the most intense peak of Pd appears at 36.65° represent 100 plane of hexagonal system JCPDS file no 72-0710 than 111 plane of fcc system, as evident from JCPDS data, it can be inferred that hexagonal Pd is generated when the reaction is carried out in aqueous ethanol as the selected medium for reduction.
of $\text{Pd}^{2+}$. Notably, for samples synthesized from 40% ethanol solvent, an intense peak appears at ca 36.50° for 100 plane of hexagonal Pd. Thus it can be concluded that on increasing ethanol in the reaction medium gradually hexagonal Pd is generated in the process. It would be worth to mention here that the change in crystal structure from cubic to hexagonal is associated with the gradual decrease in the rate of reduction of $\text{Pd}^{2+}$ on increasing ethanol in the reaction mixture, as evident from the absorbance values obtained after a definite interval of time from the start of the reaction, as presented in figure 1(a).

3.3. TEM analysis

The TEM images of the PVA-encapsulated Pd nanoparticles synthesized from aliquot after 6 min of metal reduction and synthesized from different solvents are shown in figure 3. It is apparent that palladium nanoparticles formed in aqueous ethanol solvents and water are mainly spherical and well separated. The size distribution and the average particle size are shown in the histogram (inset) of the corresponding TEM images. Alcohol containing media always furnish global particles. The change in the average diameter of spherical Pd nanoparticle on addition of ethanol to the aqueous synthesizing mixture is small but definite. On gradual addition of ethanol in the synthesizing aqueous medium, a gentle increase in the average diameter of spherical Pd nanoparticles is revealed from TEM data. In pure water Pd nanoparticles are usually wrapped with solvated PVA molecule according to scheme 1. On addition of ethanol, $\text{H}_2\text{O}$ is replaced gradually by ethanol because of purely statistical reason. Moreover the mobility of particles increases due to lowering of the viscosity of the medium, resulting increase of particle size.
3.4. FTIR-spectra analysis

The spectra of the PVA along with other components including and excluding palladium nanoparticles (considered after 24 h reaction) are shown in figure 4. In the blank spectrum of PVA without PdCl₂, the band at 3450 cm⁻¹ is assigned to the stretching mode of the PVA hydroxyl group. It is known from the literature [40, 41] that for polymer coated metal nanoparticles the functional group plays vital role to protect metal nanoparticles via the co-ordination of the functional groups to the particle surface. In addition to the steric stabilization effect exerted by the polymer chain, it is also responsible for protection and stabilization. So the shift of the assigned band (3450 cm⁻¹) towards lower frequencies for the sample containing Pd nanoparticle, is due to the interaction of the hydroxyl group with the negatively charged surface of palladium nanoparticles, which are supposed to adsorb chloride ions preferentially at their outer surface [42].

FTIR study of residue containing nano Pd obtained using pure water as reaction medium shows two peaks at around 3310 and 3438 cm⁻¹. The small first peak at 3310 cm⁻¹ which is absent in pure PVA sample, is attributed to O–H stretching frequency of bonded H₂O molecules (present in small quantity in the solid sample) with Pd nanoparticles. The second peak is assigned to the O–H stretching frequency of PVA bonded with Pd and/or H₂O. As the amount of ethanol increases in the initial reaction mixture the wave number of the 1st peak tends to disappear while that of 2nd peak increases for the Pd-PVA nano-composite. On addition of alcohol in the synthesizing medium, PVA gets less number of water molecules for its interaction. Thus overall –OH interaction of H₂O-PVA decreases with a result of increase in wave number/frequency on addition of alcohol. The curve (d) of figure 4 also shows that in Pd/PVA obtained using 40% ethanol, there is no additional peak due to bonded H₂O molecules. This can be explained by considering the fact that as the ethanol increases it withdraws H₂O molecule from the matrix of PVA. As a consequence of this, the 2nd peak shifted to the higher wave number following the order Pd-PVA (from water, 3424 cm⁻¹) < Pd-PVA (from 10% ethanol-water, 3439 cm⁻¹) < Pd-PVA (from 40% ethanol-water, 3442 cm⁻¹).

3.5. Analysis of the electrocatalytic activity of palladium nanoparticles and the role of solvent in synthesis

Figure 5 presents similar blank cyclic voltammograms (CVs) of the electrodes constructed using Pd nanoparticles synthesized from water and representative aqueous organic mixtures.
as reaction media, in 1 M NaOH solution in the scan range between −0.65 V and +0.5 V at the scan rate of 50 mV s$^{-1}$ at room temperature. The profile at the inset for bare Ni in anodic direction shows a peak at potential around +0.49 V as usual indicating for the conversion Ni(OH)$_2$ to NiOOH [43, 44]. In the same CV profile the cathodic peak at around +0.4 V is due to the conversion of NiOOH to Ni(OH)$_2$ as reported in other studies [44]. It appears from the CVs of Ni/Pd(1–5) electrodes in 1 M alkali that in anodic direction the first peak in the potential range of −0.03 V to +0.1 V for different electrodes signifies the formation of MOH according to the reaction:

$$M + \text{OH}^- \rightarrow \text{MOH} + e^- \quad (M = \text{Pd, Ni}).$$

The second anodic peak at ca +0.25 V arises due to formation of Pd(OH)$_2$ from nano-Pd on the electrode-surface according to the following reaction:

$$\text{PdOH} + \text{OH}^- \rightarrow \text{Pd(OH)}_2 + e^-$$

and

$$\text{Pd} + 2\text{OH}^- \rightarrow \text{Pd(OH)}_2 + 2e^-.$$

In the same CV profile the cathodic peak at ca −0.24 V is due to simultaneous reduction of Pd(OH)$_2$ to Pd(0) and Ni(II) to Ni(0) as reported elsewhere [44]. All the Ni/Pd(1–5) exhibit a similar characteristic CV pattern in the zone of redox conversion of Ni(OH)$_2$ to NiOOH but they differ in zone III there, an extra cathodic peak is obtained for all these modified electrodes during reverse scanning. A careful analysis also reveals that a notable anodic charge flows just before the onset of Ni(OH)$_2$ to NiOOH formation over and above that observed for bare Ni, indicating simultaneous oxidation of Pd(0) to Pd(OH)$_2$.

$$\text{Pd} + 2\text{OH}^- \rightarrow \text{Pd(OH)}_2 + 2e^-,$$

along with the existing anodic process on the bare Ni

$$\text{Ni} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 + 2e^-.$$

Some of the generated Pd(OH)$_2$ molecules undergo transmetalation reaction

$$\text{Pd(OH)}_2 + \text{Ni} = \text{Ni(OH)}_2 + \text{Pd}$$

helping generation of more NiOOH for the modified electrodes than that obtained for bare Ni in zone I according to the well known reaction equation

$$\text{Ni(OH)}_2 + \text{OH}^- = \text{NiOOH} + \text{H}_2\text{O} + e^-.$$

From this increased peak current density in both zone I and II for the modified electrode the Ni/Pd(1–5) than pure Ni. Notably, the reaction in zone II is conversion of NiOOH to Ni(OH)$_2$.

Figure 6 shows the CVs for electro oxidation of 1 M ethanol in 1 M NaOH on all the modified electrodes in the scan range of −0.5 V to +0.15 V at 50 mV s$^{-1}$. The profile show typical behaviour observed for ethanol oxidation [44, 45]. Each profile shows two anodic peaks. The CV profile of bare Ni suggests that bare Ni does not show any significant oxidation of alkaline ethanol in the potential region studied. On the other hand, Ni/Pd(1–5) electrode shows profound oxidation of ethanol as it appears from large forward and backward peak current densities ($i_F$ and $i_B$). Peak current ($i_F$) for forward scan of figure 6 shows the order which is not expected for these electrodes on the basis of embedded nanoparticle size alone. Since all the electrodes have different catalyst loading so the following order of $i_F$ is expected Ni/Pd(1) > Ni/Pd(2) > Ni/Pd(3) > Ni/Pd(4) > Ni/Pd(5). But this is not found to be the case (vide figure 6 and table 1). It is observed that $i_F$ values synthesized from different solvents follow the trend Ni/Pd(1) > Ni/Pd(4) > Ni/Pd(5) > Ni/Pd(3) > Ni/Pd(2). Since all the electrodes have different catalyst loading so the anomalous result may originate from Pd(0) loading on the Ni-substrates. In order to verify this, conventional CVs are there by converted to current (A/mole of Pd) versus potential (V) plot figure 7 where effect of catalyst loading is rationalised. The corresponding values follow the order: Ni/Pd(1) > Ni/Pd(5) > Ni/Pd(4) > Ni/Pd(3) > Ni/Pd(2). When
ethanol is added to the aqueous synthesizing medium, it interacts more with H₂O than PVA, because of more affinity and statistical reason. So PVA gets less number of water molecules to interact. The functional group of PVA (i.e. OH group) is therefore selectively more available to interact with Pd nanoparticle which is seemingly wrapped with Cl⁻ ions. Pd nanoparticles being more wrapped (covered) by PVA molecule is less available for reactant ethanol molecule during its electrochemical oxidation. Thus the electrochemical rate of reaction viz current density at a given potential and peak current density decrease for Pd particle synthesized from 10% aqueous ethanol in comparison to that synthesized from water. So, it may be expected that less would be the peak current density, greater the % of alcohol in the synthesizing medium. Ethanol also forms H-bonds with the Pd(0) encapsulating aqueous PVA molecule as presented in scheme 1. Therefore, it exerts initially a more difficult environment to the reactants to approach to the electrode. So, i_p and i_b values for Pd particles synthesized from aqueous mixture of 10% ethanol are found to be the worst in catalysis, although the corresponding particle diameter is smaller. Now, on further addition of alcohol to (10% ethanol + 90% H₂O) mixture, PVA becomes less rigid around Pd nanoparticles. So, the interaction of PVA-Pd cluster decreases affording a relatively less encapsulated Pd nanoparticle for the reactants to approach. Thus the current density and hence electrocatalytic activity increases for particles synthesized from aqueous ethanol containing 20% alcohol solvent mixture. Greater the % of alcohol in the synthesizing aqueous ethanol medium less would be the effect encapsulation of PVA and thus current density and electrocatalytic property is increased. The whole mechanism is represented by scheme 1.

3.6. Chronopotentiometry

Chronopotentiometry profiles of Ni/Pd(1–5) electrodes are presented in figure 8. These are obtained by drawing constant current density of +40 μA cm⁻² through the electrodes immersed in 1 M EtOH in 1 M NaOH. Three regions of CP profiles (figure 8) are distinctly noticed for the electrodes in the given scale as observed in our earlier study [44, 45]. In the lower potential range, the potential increases very sluggishly with time and then in the second region, a sharp increase occurs leading to a third and steady region at the potential ranging from 0.41 V to 0.43 V. The first region signifies the region of potential where mainly dehydrogenation and slow poisoning occur in the process of ethanol oxidation. The second region signifies fast coverage of electrode by carbonaceous species making the dehydrogenation step less important. The third steady region indicates the oxidation of ethanol on the modified surface containing Ni(OH)₂ and NiOOH, which generate in the high potential region (E⁰(Ni³⁺/Ni²⁺) = 0.49 V) [43]. So better the catalytic capability of electrode, more time it would enjoy at the relatively lower potentials without modification of the surface. The time required to reach the steady current at

### Table 1

The peak current densities (i_p and i_b), peak potentials (E_p and E_b), embedded nanoparticle diameter (d), catalyst loading (c) and other derived parameters from first cycles of repeated CV study of Ni/Pd(1–5) electrodes in 1 M ethanol in 1 M NaOH at a scan rate of 0.05 V s⁻¹.

| Electrode | c (mmol cm⁻²) | d (nm) | i_p (mA cm⁻²) | E_p (V) | i_b (mA cm⁻²) | E_b (V) | i_p/i_b | i_p (A mol⁻¹) | i_b (A mol⁻¹) |
|-----------|---------------|-------|-------------|--------|--------------|--------|--------|-------------|-------------|
| Ni/Pd(1)  | 1.16 × 10⁻⁴   | 2.05  | 1.986      | −0.190 | 0.931        | −0.299 | 2.133  | 17120.69    | 8025.86     |
| Ni/Pd(2)  | 1.071 × 10⁻⁴  | 2.31  | 0.482      | −0.149 | 0.313        | −0.257 | 1.540  | 4500.47     | 2922.50     |
| Ni/Pd(3)  | 1.285 × 10⁻⁴  | 2.75  | 0.900      | −0.199 | 3.245        | −0.380 | 0.277  | 7003.89     | 25252.92    |
| Ni/Pd(4)  | 1.16 × 10⁻⁴   | 2.85  | 1.322      | −0.214 | 0.378        | −0.331 | 3.497  | 11396.55    | 3258.62     |
| Ni/Pd(5)  | 0.879 × 10⁻⁴  | 2.98  | 1.241      | −0.205 | 1.477        | −0.368 | 0.840  | 14118.32    | 16803.19    |
high potential is therefore a measure of the resistance offered by the electrode against poisoning and designated by the transition time, $\tau$. Here in the study, $\tau$ (presented in second with in parentheses) increases in the following order: Ni/Pd(3) (325 s) < Ni/Pd(4) (610 s) < Ni/Pd(2) (655 s) < Ni/Pd(5) (700 s) < Ni/Pd(1) (6935 s). This reflects the order of resistances offered by the different electrodes or the stability of the electrodes against poisoning during electro-oxidation of ethanol. This shows that the Ni/Pd(1) offers the strongest resistance against poisoning among the electrodes studied and the order of stability against poisoning increases with the decrease in the diameter of the nanocrystallites used to construct the electrodes. Exception is found for particles synthesized from water and 10% ethanol where the encapsulation of Pd cluster by PVA is greater.

3.7 Chronoamperometry

Figure 9 represents chronoamperometric profiles of the electrodes at potential +0.15 V. It is found that the current density produced by electrode Ni/Pd(1) is the highest among the Ni/Pd(1–5) electrodes. It is clear from figure 9 that steady current density (expressed in within parenthesis) of the presented electrodes decreases in the order: Ni/Pd(5) (10.25) > Ni/Pd(4) (7.65) > Ni/Pd(3) (4.25) > Ni/Pd(2) (2.59). Thus Ni/Pd(1) electrode shows considerably improved performance in catalytic activity as well as optimum poisoning tolerance capability compared to others. It should be noted that the order of catalytic activity as revealed by the steady current density is in agreement with the CV and CP studies. Now the steady current density ($Y$, vol.% of co-solvent $X$) profile and the corresponding fitted ($R^2 = 0.991$) equation: $Y = 0.765 + 0.1463X + 0.00235X^2$ reveal that the current density for Pd nanoparticles synthesized from ethanol-water system would exceed that from water at composition of 63 vol.% of ethanol presented in figure 10. The increase in current density in water-ethanol media is due to decreased rigidity of PVA matrix which makes the reactant more available towards Pd nanoparticles.

4. Conclusions

Electrocatalytically active palladium nanoparticles have been synthesized successfully at room temperature and completely green method by the reduction of $\textit{in situ}$ generated $\text{K}_2\text{PdCl}_4$ in aqueous alcohol in presence of PVA. UV–Vis spectroscopic, TEM, and XRD studies show that Pd nanoparticles are in nanosize domain. The catalytic property of the electrodes constructed from the particles synthesized from different aqua-organic solvents shows the sequence: Ni/Pd(1) > Ni/Pd(5) > Ni/Pd(4) > Ni/Pd(3) > Ni/Pd(2), indicating $\text{H}_2\text{O}$ is the effective solvent for synthesis of better Pd catalyst for oxidation of ethanol due to formation of the smallest nanoparticles in the system of solvents studied. However, the current density of Pd nanoparticles synthesized from ethanol-water mixture containing 63 vol.% of ethanol may exceed theoretically to that from water. Moreover, the extent of encapsulation of PVA to Pd nanoparticles can be decreased by increasing the co-solvent composition of aqua-organic solvent mixture, as reflected in the increased catalytic property of the synthesized particle from the highest percentage of alcohol studied.

Acknowledgments

The authors like to thank Jadavpur University (UGC CAS program) for all financial and instrumental support.

References

[1] Seigel R W 1993 Mater. Sci. Eng. B 19 37
[2] Teranishi T and Miyake M 1998 Chem. Mater. 10 594
[3] Guo S and Wang E 2011 Nano Today 6 240
[4] Srivastava S K, Yamada R, Ognino C and Kondo A 2013 Nanoscale Res. Lett. 8 70
