



Original scientific paper

Electrodeposited palladium as efficient electrocatalyst for hydrazine and methanol electrooxidation and detection

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Abstract

Electrodeposited palladium was used as an electrocatalyst for electrochemical oxidation of hydrazine and methanol and the development of a sensitive platform for their detection. The electrochemical behavior of the electrode was evaluated by cyclic voltammetry (CV), while electroanalytical properties were determined by differential pulse voltammetry (DPV). The electrodeposited Pd catalyst exhibited good electrocatalytic activity towards oxidation of hydrazine in neutral solution and methanol oxidation in alkaline solution. Under optimized DPV conditions, the electrodeposited Pd electrode shows good sensing capability for hydrazine and methanol detection.

Keywords

Sensitivity; differential pulse voltammetry; electroanalytical properties

Introduction

The interest in fuel cells has been growing over the past few decades, particularly for low-temperature fuel cells, since they can be used in portable electronic devices, electric vehicles, or stationary power supplies. Direct methanol fuel cells (DMFCs) are promising power sources, and as such, they demand highly efficient electrocatalysts for methanol electrooxidation. It was shown that Pd is an appropriate replacement for Pt because of its lower cost, higher tolerance against CO-like species, and better stability [1]. In addition, the choice of potential fuels is varied, and among them, hydrazine is of interest due to its large theoretical energy density, ease of storage and transport, and faster overall oxidation kinetics compared to the carbon-containing compounds [2].

It has been known that organic compounds, such as formaldehyde, isopropanol, methanol, hydrazine, are volatile and harmful to human health. To detect these compounds, many research groups investigate and have already established sensors with rapid response rates, excellent stability, and selectivity. Nanostructures could be promising and effective electrodes for sensing applications and the detection of various chemicals. Electrodeposition is one of the most efficient methods for the

preparation of metals or their alloys as nanostructures with appropriate composition and morphology. This rapid and facile technique provides nucleation and growth of metal nanoparticles with different sizes and shapes depending on applied potential, current, time, or concentration of the solution. In recent years the electrochemical detection of hydrazine or methanol using Pd nanostructures has been reported in the literature. The highly dispersed and ultrafine carbon-supported Pd nanoparticles (Pd NPs) catalyst was synthesized by the NaBH_4 reduction method in the presence of ethylenediamine-tetramethylene phosphonic acid (EDTMP) [3]. This Pd/C catalyst exhibited a significant electrocatalytic performance for hydrazine oxidation in 0.05 M H_2SO_4 . Rastogi et al. investigated Pd NPs immobilized on organic-inorganic hybrid nanocomposite material coated on a GC electrode as electrocatalyst in the oxidation of hydrazine and its amperometric sensor [4]. Using pulsed electrodeposition technique, Pd species were deposited on the multi-walled carbon nanotubes dispersed in Nafion membrane to catalyze the electrooxidation of hydrazine and investigate their electroanalytical properties [5]. Zhang *et al.* reported the preparation of Pd NPs loaded on cobalt nanoparticles wrapped in nitrogen-doped carbon nanotubes for hydrazine determination [6]. Considering electrochemical methanol sensors, research is directed toward developing electrode materials that can electrochemically oxidize methanol at low potentials with high selectivity, providing high sensitivity. Tao *et al.* proposed an electrochemical methanol sensor based on palladium-nickel nanoparticles dispersed onto the surface of the silicon nanowires [7]. This composite electrode shows good electrooxidation capability for methanol, and because of that, it can be used for its detection. Electrochemical sensor for the determination of methanol-based on Pd NPs supported on Santa Barbara amorphous-15- PrNH₂EtNH₂ (PdNPs@SBA-15-PrEn) is synthesized as well [8].

The aim of this paper is to prepare the electrode applying the electrochemical deposition of Pd without any additives in a simple one-step procedure and to examine its electrocatalytic activity and sensitivity in hydrazine and methanol oxidation. The sensing parameters such as sensitivity and detection limits are determined by means of differential pulse voltammetry (DPV) measurements.

Experimental

All electrochemical measurements were performed using Volta Lab PGZ 402 (Radiometer Analytical, Lyon, France). A conventional three-electrode system was employed, including a gold rotating disk electrode (Au) electrode (geometric surface area 0.196 cm²) as the working electrode, Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A mirror-like polished Au electrode was prepared as previously stated [9]. The electrochemical deposition was performed without any additives in a simple one-step procedure at a potential of -0.16 V within 100 s and 1000 rpm at room temperature from deaerated 0.1 M NaCl solution containing 30 mM PdCl_2 as was previously described [10]. In DPV measurements, the accumulation of the hydrazine at the working electrode was carried out for 0.2 s at -400 mV and 0.2 s at -600 mV for methanol. After that, the potential was scanned at a scan rate of 0.125 mV s⁻¹, pulse amplitude of 50 mV, $f = 5$ Hz and step value 2 mV. All reagents were of analytical grade and purchased from Sigma-Aldrich. All solutions were prepared using nanopure water supplied by a Milli-Q system (Millipore®) with resistivity ≥ 18.2 M Ω cm. Electrochemical measurements were performed under N_2 atmosphere at ambient temperature.

Results and discussion

Electrochemical oxidation of hydrazine

A complete characterization of prepared Pd catalyst involving structural, morphological, and surface studies, was previously reported [10]. According to SEM measurements, a simple

electrochemical deposition process without surfactants created the morphology of nanorods with a diameter of ~ 5 nm and an aspect ratio of ~ 8 . A clear rod shape was resolved by TEM image.

It is well known that the electrode surface area and reactant concentration affect the current. In the presented work, one electrodeposited Pd electrocatalyst was examined and it is reasonable to assume that the electrochemically active surface area is the same in all experiments. If the other parameters such as temperature and the viscosity of the solution remain constant, the current is proportional to the reactant concentration. Because of that, the results were given per geometric surface area or just as current intensity.

The electrocatalytic activity of electrodeposited Pd in the oxidation of 0.5 mM hydrazine was investigated in 0.1 M K_2SO_4 (pH 7) at 100 mV s^{-1} as is presented in Fig 1a. Neutral solution was selected as a blank electrolyte since it has been shown that the electrooxidation of hydrazine is more favored under neutral conditions regarding alkaline medium [11,12]. One anodic peak for hydrazine oxidation at 80 mV in the forward scan can be noticed. The absence of a current peak in the backward scan implies that the electrooxidation of hydrazine is an irreversible process that occurs during the positive potential scan.

It has been shown that for the oxidation of hydrazine at platinum electrodes, surface oxides are substantial to electrocatalysis [13]. To establish the necessity of surface oxides, voltammetry was conducted in the absence of hydrazine at the Pd electrode. Figure 1b shows the typical response feature of the Pd surface. The peak in the range of -700 to -400 mV is for the oxidation of the adsorbed and absorbed hydrogen. A reversible redox feature in the potential region -200 – 100 mV is ascribed to the influence of ions in a sulphate electrolyte [14] and possibly also to the effect of the metal loading [15]. As is illustrated in Figure 1b the formation of Pd oxides starts at $E > 400$ mV, which is a higher overpotential than noticed in hydrazine oxidation. So, the effect of surface palladium oxide on electrocatalytic activity of Pd catalyst should be neglected during the hydrazine electrooxidation.

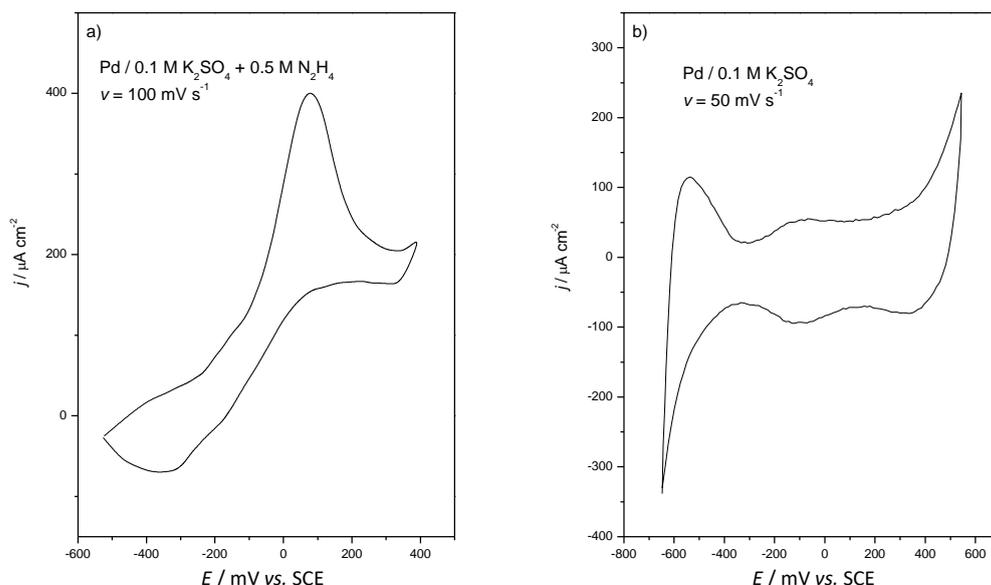


Figure 1. CV of electrodeposited Pd in 0.1 M K_2SO_4 in the presence (a) and absence (b) of 0.5 M N_2H_4 .

Voltammetric response, forward direction, of Pd electrode towards electrochemical oxidation of hydrazine was investigated as a function of scan rate (Fig. 2). With an increasing scan rate, a positive shift in the oxidation peak potential along with enhancement in catalytic current density was noticed. The plot of current density vs. square root of scan rate (Fig. 3a) showed a linear

dependency, demonstrating that hydrazine electrooxidation on Pd electrode is a diffusion-controlled process which is in accordance with the reported results [3,16].

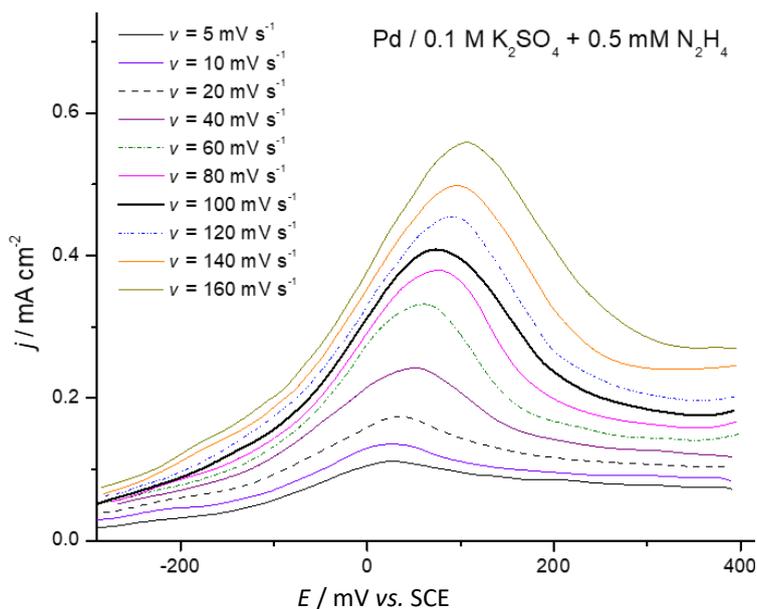


Figure 2. The forward direction of CVs obtained on Pd electrode towards 0.5 mM N₂H₄ in 0.1 M K₂SO₄ at a scan rate from 5 to 160 mV s⁻¹

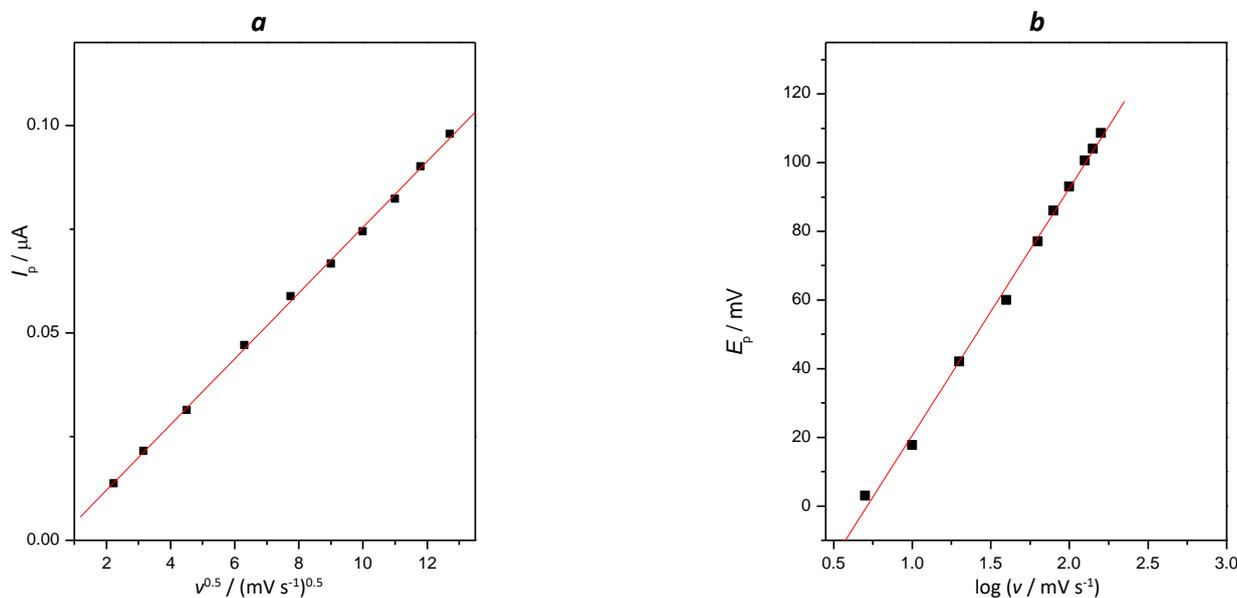


Figure 3. (a) Plot of peak current vs. square root of scan rate. (b) Plot of peak potential from the log of scan rate. Data collected from Fig. 2

The oxidation potential simultaneously shifts to positive values with a linear correlation between the peak potential and the logarithm of scan rate, as is presented in Fig. 3b. Bearing in mind that dependency, the Tafel slope was considered using the equation (1) for the irreversible diffusion-controlled process [17]:

$$E_p = b/2 \log v + \text{const.} \tag{1}$$

The slope of the dependency $E_p - \log v$ is $b/2$, and it is found to be 62 mV in this work, thus $b = 2 \times 62 = 124$ mV. The Tafel slope is $b = 59/(1-\alpha)n$ (α is the transfer coefficient; n - the number of electrons involved in the rate-determining). It is well known that the first electron transfer of hydrazine oxidation is rate-determining [4,18]. Assuming the number of electrons is 1, the transfer coefficient is estimated as 0.48, illustrating that the rate-limiting step is a one-electron transfer

process. The mechanism of hydrazine oxidation was studied electrochemically at the Pd electrode in solutions of different pHs (pH 2-11), presented in detail [19-21]. It has been shown that the mechanism of hydrazine oxidation depended significantly on the electrolyte solution and the nature of the electrodes [2,19]. Hydrazine is oxidized through the $4e^-$ process with the final product N_2 in an aqueous solution [14,18]. The first intermediate of hydrazine oxidation in aqueous solutions has been identified as the radical ion $N_2H_4^{\bullet+}$ [22] or radical di-cation $N_2H_5^{\bullet 2+}$ [19]. The formation of $N_2H_4^+$ ion was usually regarded as the rate-determining step, while other proposed intermediates are not stable [23].

Electrochemical oxidation of methanol

Figure 4 shows the voltammetric response of investigated Pd catalyst in 1 M NaOH containing 1 mM methanol at 50 mV s^{-1} . Electrodeposited Pd showed two anodic peaks for methanol oxidation at -250 mV in the forward scan and at -430 mV in the backward scan. The peak observed in the forward scan was ascribed to the oxidation of chemisorbed species coming from methanol adsorption on the surface of the catalyst in the presence of adsorbed OH^- species. The peak in the reverse scan might be caused by oxidation of freshly chemisorbed species or carbonaceous species, which are not completely oxidized in the forward scan. OH^- formation ability of a catalyst is in relation to alcohol oxidation activity. It is well documented in the literature that the kinetics of the alcohol oxidation reaction is enhanced by increasing the concentration of OH^- ions in the solution, thus causing the higher coverage of the electrode surface by OH^- species [24,25]. So, unlike hydrazine, methanol oxidation is determined by the degree of chemisorbed species originating from methanol and OH_{ad} coverage. Kinetic study of methanol electrooxidation reaction on Pd-based catalysts is well described in the literature [25,26].

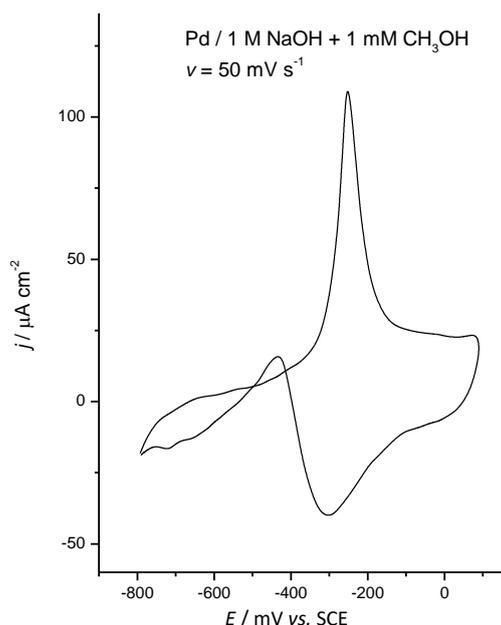


Figure 4. CV of electrodeposited Pd in 1 M NaOH in the presence of 1 mM CH_3OH at a scan rate 50 mV s^{-1}

Electroanalytical determination of hydrazine and methanol

To check the analytical performance of the electrodeposited Pd electrode in the electrochemical determination of hydrazine and methanol, DPV and square wave voltammetry (SWV) were tested. Since the DPV showed improved peak current compared to SWV the first-mentioned method was used and optimized to detect these molecules. DPV response of electrodeposited Pd catalyst towards different concentrations of hydrazine was presented in Figure 5a. With increasing hydrazine

concentration, the current of hydrazine oxidation also increases. According to Fig. 5b, the calibration plot of current vs. hydrazine concentration gives a linear dependence in the concentration range of 0.1-2 mM hydrazine. An excellent correlation coefficient ($R = 0.999$) was obtained as well.

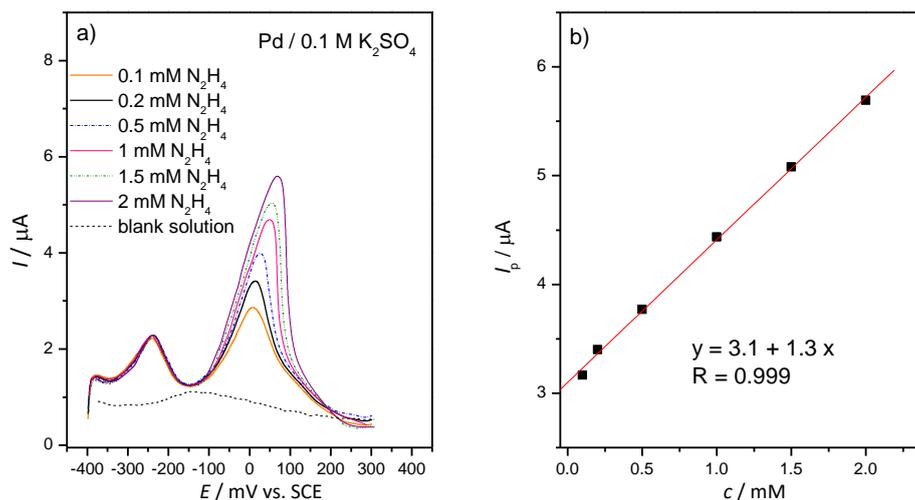


Figure 5. (a) DPVs obtained on the electrodeposited Pd electrode in the presence of increasing hydrazine concentrations. (b) Dependency of peak current on hydrazine concentration

Figure 6a shows the results of DPV obtained on the electrodeposited Pd electrode in the presence of an increasing concentration of methanol. Alkaline media were chosen because of their higher activity and poisoning resistance regarding acidic or neutral media. It can be noticed that the addition of methanol leads to a rapid and well-resolved increase of the peak currents at ~300 mV. E_p slightly shifts (~15 mV) towards more positive potentials, indicating that electrodeposited Pd shows satisfactory poison resistance from electrochemically formed intermediates.

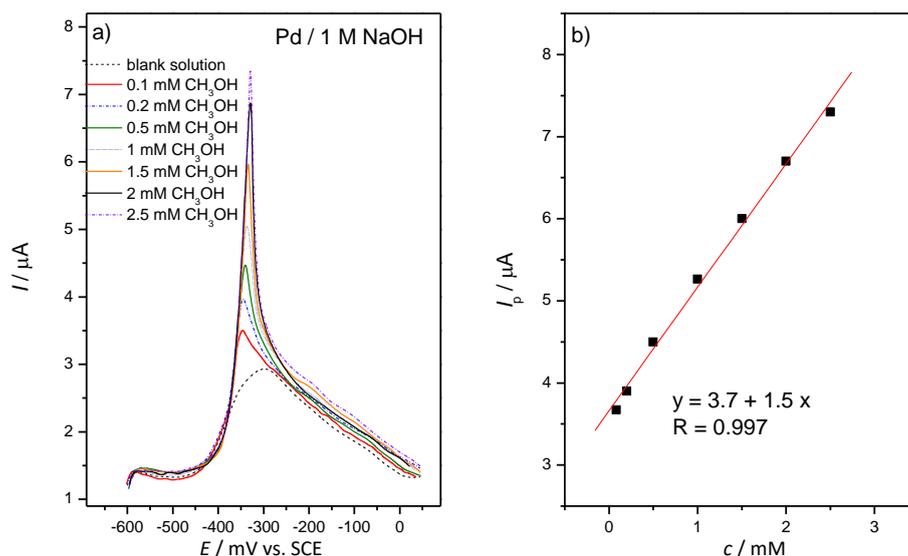


Figure 6. (a) DPVs obtained on the electrodeposited Pd electrode in the presence of increasing methanol concentration. (b) Dependency of peak current from concentration

The constructed linear dependency was used to evaluate several electroanalytical parameters. Thus, sensitivity was obtained from the slope of the calibration curve. The other electroanalytical parameters are the limit of detection (LOD) and the limit of quantification (LOQ). LOD demonstrates the lowest compound concentration which can be detected, while LOQ demonstrates the lowest concentration of compound, which can be quantitatively determined. Both LOD and LOQ were

calculated according to the equations $k' SD / b$, where $k' = 3$ for LOD and 10 for LOQ, SD is the standard deviation of the intercept and b is the slope of the calibration curve [27]. The obtained electroanalytical parameters are given in Table 1. It should be noted that the comparison of the electrochemical result is not unambiguous, as the electrochemical parameter is dependent on more than one experimental variable.

Table 1. Determination of investigated compounds by DPV

Compound	Concentration linear range, mM	Sensitivity, $\mu\text{A mM}^{-1}$	LOD, mM	LOQ, mM	R
Methanol	0.1-2.5	1.5	0.21	0.71	0.997
Hydrazine	0.1-2	1.3	0.09	0.3	0.999

The sensing capability of Pd in hydrazine detection is comparable to that established on Pd species deposited on the multi-walled carbon nanotubes dispersed in the Nafion membrane [5]. Nevertheless, the obtained LOD and LOQ values for both investigated compounds are lower than the reported data obtained on Pd nanostructures [5,8,18,28], indicating the unavoidable improvement of the electrochemical characteristic. Following this strategy, the synthesis of Pd nanostructures of diverse shapes has been extensively used. Additionally, a mixture of metals forming alloys or core-shell structures can be found in literature as an effective way of improving electrocatalytic activity. Enhancing the electrochemical activity and sensitivity towards hydrazine and methanol oxidation will be a matter of future studies.

Conclusions

Electrochemical deposition of Pd was performed without any additives in a simple one-step procedure. Electrodeposited Pd was then used as an electrocatalyst for the electrochemical oxidation of hydrazine and methanol. The electrochemical behavior of the Pd electrode reveals that the effect of surface palladium oxide should be neglected in the course of hydrazine electrooxidation. Conversely, in the case of the oxidation of methanol, surface oxides are necessary to electrocatalysis. The constructed linear dependency of I_p from hydrazine or methanol concentration was used to evaluate electroanalytical parameters. Some improvements will be a matter of future studies.

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