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Bijal Kottukkal Bahuleyan
Yanbu Industrial College

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Research article

Electrochemical Deposition of Highly Catalytically Active Palladium Nanoparticles - Application to Methanol Fuel Cell Anodes and its Kinetic Studies

Bijal Kottukkal Bahuleyan, Ph. D[1] [a]

[1] Department of General Studies, Yanbu Industrial College

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Fuel cell technology is a green and promising energy source for the future generation. Amongst all fuel cells, methanol oxidation with very low overpotential at modified electrodes is important for understanding and developing methanol fuel cell anodes. Platinum (Pt) is a well-known catalyst for the methanol oxidation reaction. However, Pt is expensive and also methanol oxidation intermediates adsorbs very strongly onto its surface. In the present study, a less expensive and highly active electrocatalyst was developed using palladium (Pd) by simple electrochemical technique. The scanning electron microscope (SEM) displays that small sized nanoparticles are in the range of 4-8 nm. The prepared material shows excellent electrocatalytic activity with quite low overpotential at room temperature. In addition, to understand the kinetics, energy of activation was determined by studying the methanol oxidation reaction at different temperature. The onset potential decrease with increasing temperature implies that the kinetics of the process improves at elevated temperature. The lowest activation energy was found to be 20 kJ/mol which is almost comparable with many Pd based materials.

INTRODUCTION

The development of fuel cell anodes with low overpotential for electro-oxidation of alcohols remain a challenge. The studies on electro-catalytic oxidation of alcohols using precious metal catalysts have attracted considerable interest.[1–5] Platinum (Pt)-based metal or alloy nanoparticles (NPs) are of great research interest in a number of areas.[6] The precious metal, Pt, is known to be a good electro-oxidation catalyst in direct alcohol fuel cells (DAFCs) as well as formic acid fuel cells (DFFCs).[7–10] However, DAFCs and DFFCs are still limited by high production costs due to heavy loading of Pt and its alloy materials. Moreover, the direct electro-oxidation of alcohols on Pt is complicated because of generation of strongly adsorbed intermediates, which are formed during the electro-oxidation reaction.[11–13] The catalytic activity of Pt metal decreases rapidly with increasing cycles due to the poisoning effect of strong adsorption of reactive intermediates onto its surface. In order to overcome these issues, research on enhancing the catalytic property of non-Pt nanoparticles has become great significance.[14–16] Increasing numbers of efforts to use non-Pt metal catalysts such as palladium to decrease the cost of the catalyst has been reported.[17,18]

Chemical synthesis of Pd NPs has been published by many researchers.[19,20] Again, disadvantage of using such chemically synthesized nanoparticles is to integrate them onto the conducting surfaces. Deposition of synthesized nanoparticles onto solid surfaces without affecting their properties remain a challenge. Supported metal catalysts with particle sizes down to a few nanometers are required for the practical applications. The important process in a heterogeneous catalytic reaction is the interaction of the chemical reactants with surface sites of the catalyst.[21]

Present study illustrates a simple template free in-situ electrodeposition process. It is possible to obtain a dense Pd NPs on surface possessing good adhesion, large surface area and mechanical integrity. Deposition of Pd NPs was carried out by reduction from solution containing palladium chloride as Pd source and KCl as a supporting electrolyte and mercaptobenzoic acid is used as a stabilizer to stabilize Pd NPs.

Electrochemically grown Pd on gold surface was characterized using cyclic voltammetric stripping analysis in acid medium. Electrochemically grown Pd on Au showed the typical nanosized palladium oxide stripping peaks. By integrating area under cathodic stripping peak, the real surface area was calculated. The electro-oxidation of methanol in alkaline medium using cyclic voltammetry (CV) and chronoamperometry (CA) at different temperatures were

a **Correspondence:** bijal@rcyci.edu.sa

analysed. From CV data at different temperatures the activation energies (Ea) were measured. The CA studies were carried out at different potentials and temperatures to calculate energy of activation values.

EXPERIMENTAL SECTION

CHEMICALS

Analytical grade (AR) chemical reagents were used for this study. Potassium chloride (Qualigen), Palladium chloride (Merck), 11-Mercaptobenzoic acid (Aldrich), Ethanol (Merck), methanol (Merck) were used as received. All standard solutions were prepared using Milli-Q (Millipore) water with a resistivity of 18 MΩ cm.[22]

ELECTROCHEMICAL INSTRUMENTATION

Model 262A potentiostat (EG & G) interconnected with a computer (with GPIB card, National Instruments) was designed for electrolysis. This experimental setup was utilised in a chronopotentiometry mode and in a two electrode configuration during the process of electrodeposition. In all electrochemical experiment, the potentiostat was configured with three-electrode (normal) configuration, Pt as counter electrode, calomel saturated electrode as reference and Pd NPs modified electrode as a working electrode.

ELECTRODE PRE-TREATMENT

Emery papers (grade 800 – 1500) were used to polish the gold electrode. It was then polished in aqueous slurries of alumina (fine progressive) varying their size from 1 to 0.3 to 0.5 µm on a microcloth. To remove the alumina particles, the electrode was then subjected to ultrasonification using Millipore water. After that, "pirana solution" (which is a mixture of 30% H_2O_2 with concentrated H_2SO_4 in a 1:3 ratio) was used to clean the system. Final thorough cleaning of polished gold wire electrode was carried out using distilled water and then rinsed in Milli-Q water. The potential cycle of the electrode was adjusted between -0.5 and 1.4 V at a scan rate of 200 mV/s in 0.1 M H_2SO_4. It was continued to 20 cycles for effective electrochemical cleaning.[19]

ELECTRODEPOSITION OF Pd NPs

The equal volume proportions of 1M KCl (in water) and 20 mM mercaptobenzoic acid (in ethanol solution) were mixed with 10 mM solution of $PdCl_2$. The clear solution obtained was utilized as electrolyte for further deposition. The potential of -0.7 V was applied to reduce the palladium ions onto the gold surface.[23]

CYCLIC VOLTAMMETRY STUDIES

Methanol oxidation reactions were carried out using cyclic voltammetry. Cyclic voltammetry studies were conducted at different concentrations from -600 mV to +600 mV vs SCE. CV results reported here were either 2 cycles or 200 cycles data. The experiments were carried out in order to understand the behaviour of a fresh and clean electrode in the beginning of the scan, information that could be obtained from the 2nd cycle. The information on any possible adsorbed intermediates, formed during the methanol oxidation, contaminating the surface could be gathered from the 200th cycle CV.[24]

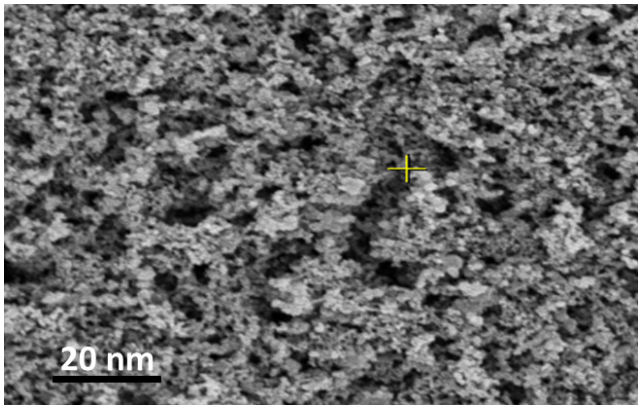

Figure 1. SEM image of electrochemically deposited Pd NPs

SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

SEM images were taken using HITACHI S4200 microscope at an accelerating voltage of 10 kV. Prior to SEM analysis, the sample was coated with platinum/gold using an Edwards S150B sputter coater.

RESULTS AND DISCUSSION

The scanning electron microscopy was carried out to understand the morphology of the deposited Pd NPs. The SEM image displays well dispersed nanoparticles with uniform morphology having particle size in the range 4-8 nm as shown in Figure 1. In addition, these nanoparticles possess porous structure which is highly desirable for the electrocatalysis.

The cyclic voltammetry was used to determine the real electrochemically active surface area of the Pd NPs in 0.5 M H_2SO_4 by measuring the charge associated with the cathodic monolayer Pd oxide stripping peak. The oxide/hydroxide stripping voltammetry is extensively used for palladium electrodes. For polycrystalline palladium, charge corresponds to the desorption of monolayer of palladium oxide is 424 µC cm^{-2}. The true surface area is calculated by measuring the charge of the modified electrodes in acidic or alkaline solution and dividing it by the actual charge value, from which the roughness factor can be determined.

$$\text{Roughness factor} = \text{True surface area} / \text{Geometric area}$$

Figure 2 shows the CV in 0.5 M H_2SO_4 for Pd deposited on Au and graphite. It shows the typical cyclic voltammogram of a palladium electrode exhibiting the characteristic peaks of palladium oxide formation and stripping in sulphuric acid solution. The true surface area of palladium electrode can be determined by measuring the charge under the palladium oxide-stripping peak.

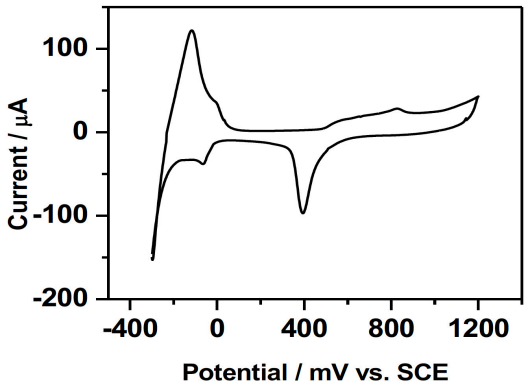

Figure 2. Cyclic voltammogram of palladium on gold electrode in sulphuric acid medium.

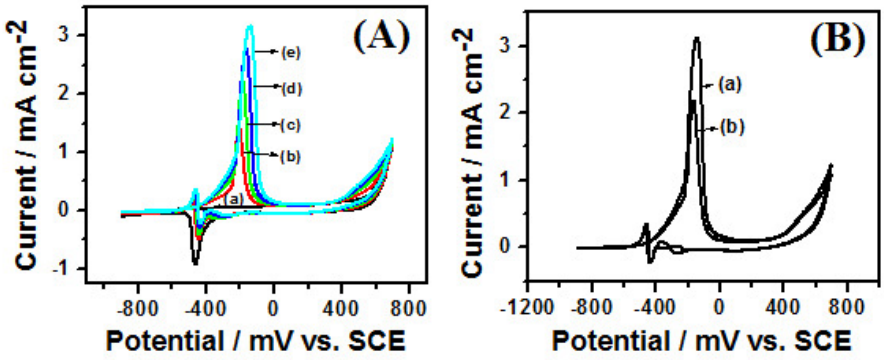

Figure 3. (A) Methanol oxidation of Pd NPs in alkaline medium and (B) Stability of the Pd NPs in alkaline medium towards methanol oxidation reaction

ELECTRO-OXIDATION REACTIONS WITH POROUS Pd NPs

Pd is known to catalyse the methanol oxidation reactions in alkaline medium. The electrocatalytic activity of Pd for methanol is evaluated in 0.5 M NaOH. Figure 3A shows the CVs for the Pd NPs surface in 0.5 M NaOH with different concentrations of methanol. Concentration of methanol was increased in steps of 0.15 M. With increasing concentration of methanol, the oxidation current also increases. The current density for the methanol oxidation was about 3.2 mA cm^{-2} for Pd NPs in 0.6 M methanol. The open circuit potential, onset potential and peak potentials were found to be -536 mV, -496 mV and -143 mV vs SCE, respectively. The high current densities and low overpotential for the methanol oxidation indicate that the Pd NPs act as good catalysts for electro-oxidation reactions. Figure 3B shows the CVs for the 0.6 M methanol oxidation for the first and 200th cycle. Upon cycling, about 25% of the current decreases. This shows that the trapping of intermediates inside the porous structure of deposited Pd NPs.

REACTION KINETICS: ACTIVATION ENERGY (Ea) AND TAFEL PLOT ANALYSIS FOR METHANOL OXIDATION REACTION

To determine the activation energy for the methanol oxidation reaction, temperature dependency studies have been carried out in alkaline medium. Figure 4 displays the cyclic voltammograms for methanol oxidation using Pd NPs electrode at different temperatures. It was observed that the methanol oxidation currents increase with the temperature. The onset potentials for the methanol oxidation decreases with increasing potential which indicates that the decrease in activation energies for methanol oxidation at higher temperatures due to the higher catalytic activity.[25–27]

A logarithmic plot of current (log i) against inverse temperature (1 / T) indicates an Arrhenius plot and such plots are often used to study the rates of chemical reactions by analysing the effect of temperature. Generally, an Arrhenius plot gives a straight line for a single rate-limited thermally activated process. From this, the activation energy can be calculated using the slope = -Ea/(2.3R).[28–30]

Figure 5 shows the Arrhenius plots for methanol oxidation on Pd NPs in 2.0 M CH_3OH + 0.5 M NaOH aqueous solution at different potentials, where i is the current at a scan rate of 100 mV s^{-1} and a very good linear relationship can be observed from these plots. This indicates that the acti-

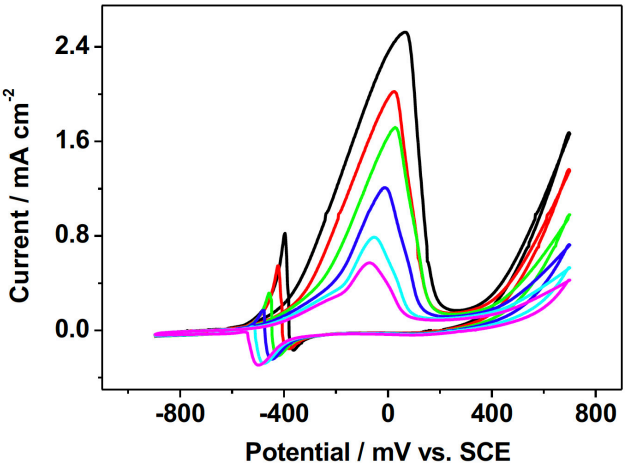

Figure 4. Temperature dependence studies for Pd NPs on gold for methanol oxidation

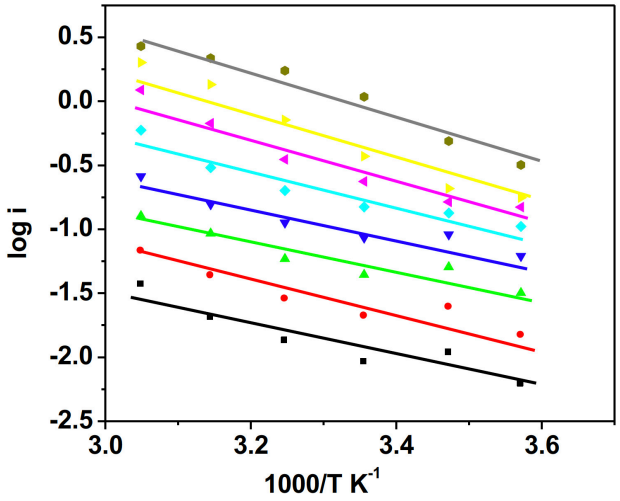

Figure 5. Arrhenius plots of Pd NPs electrode for Methanol Oxidation Reaction Potential

vation energy allows the reaction to proceed under milder conditions. In this condition a long term stability of the catalyst has achieved. It is evident that the activation energy decreases with increasing temperature. This may be due to the increasing rate of the reaction with increasing temperature.

The activation energy values for methanol reactions are given in the Table 1. It was found that activation energy is proportional to the potential applied. When the potential is decreased from -200 mV to -450 mV the activation energy also decreased from 35.2 kJ/mol to 20 kJ/mol as shown in Table 1. This shows that the methanol oxidation reaction on Pd NPs is thermodynamically feasible.

CONCLUSION

In the present study, the Pd NPs were electrodeposited by applying a constant potential in an electrolytic medium containing thiol which acted as a stabilizer. The SEM micrograph showed the well dispersed highly porous surface of the Pd NPs. Electrochemical stripping voltammetry confirmed the large surface area of the Pd NPs which is highly desirable for the electrocatalysis. The high surface area Pd electrodes have been utilized for the methanol, electro-oxidation reactions in alkaline medium. Developed electrode displays excellent electrochemical activity. Alcohol oxidation at different temperatures was calculated. The activation energy values for methanol from Arrhenius plots were calculated and the characteristics imply that they are highly catalytically active.

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Table 1. Energy of activation values at different potentials for Pd NPs for methanol oxidation

Potential (mV)	Activation Energy, E_a (kJ mol^{-1})
-200	35.2
-250	41.3
-300	33.9
-350	25.3
-400	20.1
-450	20

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