Pulsed Electrodeposition Of Palladium In 1-butyl-3-Methylimidazolium Chloride Ionic Liquid Medium For The Application In Proton Exchange Membrane Based H_2 Sensors

E. Jayanthi[a], N. Murugesan[b], and C. Ramesh[b,*]
[a]Materials Chemistry & Metal Fuel Cycle Group, Homi Bhabha National Institute, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[b]Materials Chemistry & Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
*crem@igcar.gov.in

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Abstract :

Palladium is a well-known electrocatalyst for amperometric sensing of hydrogen. Pd has higher solubility and sticking coefficient towards H_2 which facilitates better sensor performance compared to other metals. Many methods are available for the preparation of electrocatalyst such as vapour depositions, chemical reduction etc. Electrodeposition method considered to be advantageous compared to conventional methods owing to the ability to control particle size, easy preparation and devoid of wastage of catalyst. H_2 embrittlement is significant in electrodepositing Pd using aqueous electrolyte. Hence, room temperature ionic lquid (RTIL) has widely been used to avoid H_2 evolution during electrodeposition. In the present work Pd is electrodeposited on gas diffusion electrode (GDE) using C4mimCl as electrolyte. Unlike electrodeposition (ED) pulsed electrodeposition (PED) reduces diffusion layer thickness by giving on and off time pulses. This in turn reflects in the morphology of the deposit as increased effective surface area of Pd in PED. Cyclic voltammetry was carried out to study the reduction potential of Pd in C4mimCl electrolyte. Pd is electrodeposited on GDE by applying constant potential as well as pulse potential. XRD confirms the deposition of Pd and crystallite size is calculated using scherrer's formula. Pulsed electrodeposition gives higher surface area as seen from FESEM images of ED and PED Pd/GDE. Electrochemical active area of PED Pd/GDE is found to be higher than the ED. High electrochemical active area gives better sensitivity and stability in amperometric based H_2 sensors.

Keywords: electrodeposition, pulsed electrodeposition, H_2 sensor, electrochemical active area.

1. Introduction

Hydrogen embrittlement of Pd is a shortcoming in electrodepositing Pd using aqueous electrolyte (1-3). Electrodeposition using aqueous electrolyte evolves hydrogen during the deposition. Pd starts to react with H_2 once the concentration of H_2 exceeds 5 % (H_2/N_2). Pd undergoes a phase change from á to â and cause volume expansion of the Pd lattice. As a result the Pd metal loses its metallic properties and it is not desirable for sensing application (4). Hence the Pd electrodeposition using aqueous electrolyte is not preferred electrolyte. Room temperature ionic liquid electrolytes have several advantages such as higher electrochemical window(5), low vapour pressure(6) and no hydrogen evolution. Pd electrodeposition using 1-butyl-3-methyl imidazolium ionic liquid electrolyte was reported in our earlier studies(7). Pulsed electrodeposition offers many advantages than the conventional electrodeposition technique in terms of size, shape, porosity, agglomeration and adhesion. For the application of hydrogen sensing, high surface area of a catalyst is required to increase the rate of the reaction and also for enhanced life time of the sensor(8). Other techniques like screen printing or vapour deposition techniques deposits higher amount of catalyst but the amount used for sensing are only 25 % of the total surface area of the

catalyst(9). So in order to get a high surface to volume ratio of the catalyst pulsed techniques have been used. In the present study we reported the PED of Pd from 1-butyl-3-methylimidazolium chloride. Before the PED, redox behaviour of Pd is studied by performing cyclic voltammetery in $PdCl_2$/C4mimCl electrolyte. Electrodeposited Pd/GDE and pulsed electrodeposited Pd/GDE is reported for comparison. The crystal structure and microstructure of Pd/GDE is studied by x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Electrochemical active area of electrodeposited and pulsed electrodeposited Pd/GDE is measured.

2. Experiment

2.1. Pulsed electrodeposition of Pd from $PdCl_2$/ 1-butyl-3-methylimidazolium chloride ionic liquid electrolyte

Cyclic voltammetry (VMP-300 of M/S Biologic, France) was carried out in 3 mM solution of $PdCl_2$ in C4mimCl electrolyte with the three electrode cell consists of GDE working electrode, glassy carbon as counter electrode and Pt wire as reference electrode respectively. Electrodeposition and pulsed electrodeposition were carried at the respective reduction potential obtained from CV. The sample was washed with acetone, dried in an oven at 60°C for 10 mins after the electrodeposition. Potential vs. time plot for ED and PED is shown in Fig.1.

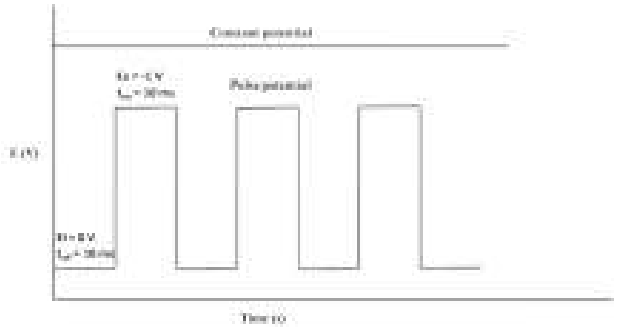


Fig.1. Potential vs time plot

2.2. Characterization of electrodeposited and pulsed electrodeposited platinum

Field emission scanning electron microscope (FEI Helios Nanolab 600i) is used for understanding the morphology of the deposit. Crystal structure was investigated by X-ray diffraction (M/s. Bruker D8, and Germany). Crysallite sizes of the deposits were calculated using scherrer's formula.

2.3. Electrochemical active surface area measurement

Membrane electrode assembly (MEA) is placed in sensor housing polycarbonate discs. These polycarbonate discs have a provision for both gas inlet and outlet. Argon was passed at one side for which the active area to be measured and H_2 was passed another side. Cyclic voltammetry (CV) was performed using potentiostat (VMP-300 of M/S Biologic, France). In CV the following parameters were set; potential used for scanning is between 0 and +1 V at the scan rate of 10 mV/s. The plot of CV is converted to I vs. time plot and the plot is integrated between 1 and +0.4 V. Electrochemical active area was calculated using the equation given below.

$$\text{Electrochemical active area } (m^2/g) = \frac{\text{Charge } (\mu C/m^2)}{210\ (\mu C/m^2) \times \text{Pt loading } (g/m^2)} \quad \text{---(1)}$$

210 ($\mu C/m^2$) is the charge produced by the oxidation of one molecule of H_2 on polycrystalline Pt in 1 m^2 area.

3. Results and discussions

3.1. Cyclic voltammetry studies of Pd from $PdCl_2$/C4mimCl ionic liquid

The electrochemical window of C4mimCl is found to be 2.5 V as indicated in Fig.1. Cyclic voltammogram of $PdCl_2$/C4mimCl is shown in Fig.1. Figure indicates two oxidation peaks (-0.17 V & 0.2 V) and one reduction peak (-0.79 V) respectively. Pd was electrodeposited at the potential of -1 V for 1 h. Pulsed electrodeposition of Pd was carried out using the following parameters: $E_L = 0$ V, $E_U = -1$ V, $t_{on} = 10$ ms, $t_{off} = 10$ ms.

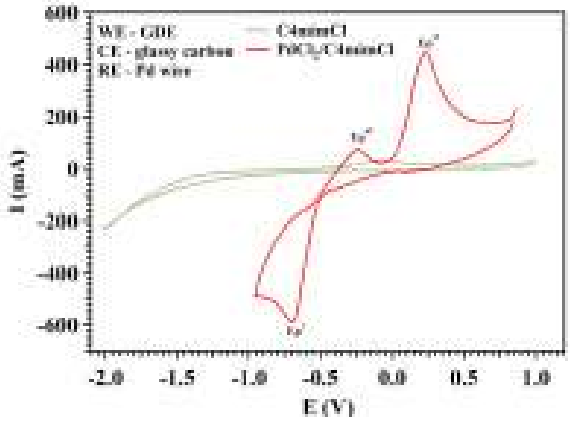


Fig.2. Cyclic voltammogram of $PdCl_2$/C4mimCl

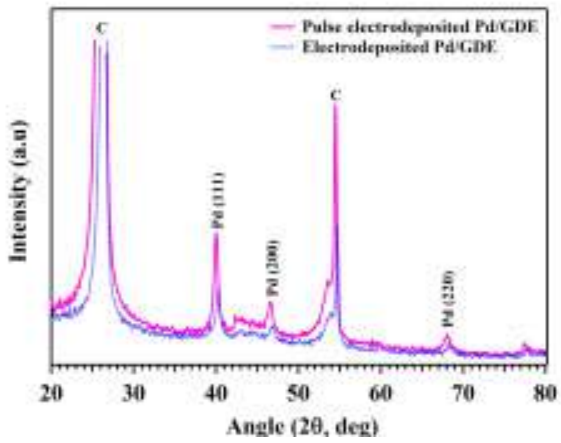


Fig.3. X-ray diffraction pattern of electrodeposited and pulsed electrodeposited Pd/GDE

3.2. X-ray diffraction studies of ED Pd/GDE and PED Pd/GDE

X-ray diffraction pattern of ED Pd/GDE and PED Pd/GDE is shown in Fig.3. The figure shows broad and low intense peak which denotes that the deposited crystals are nano in size. ED Pd/GDE and PED Pd/GDE both shows peaks at 2è values 40.199°, 46.664°, and 68.128° (JCPDS Data No: 89-4897) and is shown in Fig.3. Peaks at 2è values of 26æ% and 54æ% are correspond to graphitic carbon support of GDE (JCPDS Data No: 89-8487). The crystallites sizes of each peak were calculated and are shown in Table.1. The table indicates that the PED Pd/GDE has smaller crystallite size than ED Pd/GDE. Continuous growth of diffusion layer thickness is hampered in pulsed electrodeposition by giving t_{on} and t_{off} during deposition. During t_{off} the solution will get reorganized and ions will be available all the time near the interface. Hence, the diffusion layer thickness will be reduced and achieves finer distribution of particles.

Table 1 Crystallite sizes of Pd deposited on GDE by electrodeposition and pulsed electrodeposition in C4mimCl ionic liquid medium

Angle	ED Pd/GDE d (nm)	PED Pd/ GDE d(nm)
40.1 (111)	15	10
46.6 (200)	13	9
68.1 (220)	11	7

3.2. Microstructural investigation of electrodeposited and pulsed electrodeposited Pd/GDE

FESEM images of GDE, electrodeposited Pd/GDE and pulsed electrodeposited Pd/GDE are shown in Fig.1. FESEM image shows that the deposited Pd on GDE by ED and PED are spherical in nature. The FESEM image clearly indicates that PED Pd/GDE is uniformly distributed with less particle size compared to ED Pd/GDE.

Table 2 Electrochemical active area of electrodeposited and pulsed electrodeposited Pd/GDE in C4mimCl ionic liquid medium

Electrocatalyst	Electrochemical active area (cm^2)	Pd loading (mg/ cm^2)
Electrodeposited Pd/GDE	150	0.5
Pulse electrodeposited Pd/GDE	370	0.5

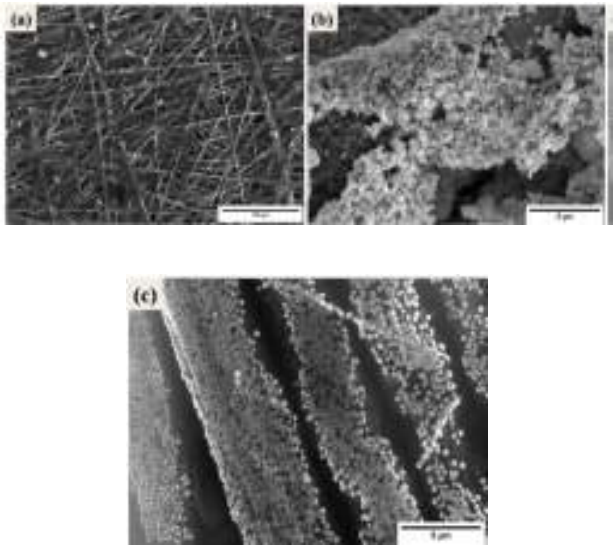


Fig.4. FESEM images of (a) GDE (b) electrodeposited Pd/GDE (C) pulsed electrodeposited Pd/GDE

3.3. Electrochemical active area measurement of ED and PED Pd/GDE

Electrochemical active area of PED Pd/GDE is higher than the ED PD/GDE (Table.2). High electrochemical active area gives better performance for amperometric H2 sensing application. The sensitivity and response time of amperometric H2 sensor depends on the three phase contact of reactant, electrode and electrolyte. High electrochemical active area of PED Pd/GDE denotes that the enhanced three phase contact which is essential for electrochemical sensors.

4. Conclusion

Pd is very selective for H2 since it has higher solubility and sticking coefficient. Pd is a better candidate for sensing H2. Pd electrodeposition using aqueous electrolyte has disadvantageous with respect H2 assisted cracking. Therefore ionic liquid electrolyte is used in the present study to avoid H2 evolution during electrodeposition. Pulsed electrodeposition offers precise control over the particle size over electrodeposition. Electrochemical active area measurement confirms that PED Pd/GDE has higher active area than ED PED Pd/GDE. PED gives finer and uniform distribution of particles as seen from FESEM image of PED Pd/GDE.

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