CHAPTER 4

ELECTROOXIDATION OF XYLITOL AT CARBON AND SINGLE WALLED CARBON NANOTUBE SUPPORTED Pd IN NEUTRAL, ACID AND ALKALINE MEDIUM

4.1 INTRODUCTION

The problem of global climate change caused by greenhouse gases and environmental pollution has necessitated to search for an alternate source of energy. Among the different energy systems, including solar power, wind power, tidal power and geothermal power, fuel cells are the most promising source of renewable and clean energy systems (Bianchini and Shen 2009, Serov and Kwak 2010).

There is currently great interest in the development of DAFCs, because the storage and use of liquid fuel is much easier than for gas fuel such as hydrogen and, in addition, reformations and purification steps are not required. Currently, the various types of fuel cells closer to commercial availability are based on direct liquid feeding principles. Fuels such as methanol, ethanol, ethylene glycol, glycerol, erythritol, Xylitol based fuel cells have studied in DAFCs. Among these methanol, ethanol, EG and glycerol have been studied extensively by a number of research group (Bianchini and Shen 2009). Recently, Pt-Ru/C and Pt/C have been studied
towards electrocatalytic activity in PEMs in alkaline membrane for polyhydric alcohols and shows the maximum power densities in the order of EG > glycerol > methanol > erythritol > xylitol (Bianchini and Shen 2009, Matsuoka et al 2005). No report on the electrooxidation of higher polyalcohols than EG or glycerol on Pd-based electrocatalysts has been reported so far.

Xylitol categorized as a polyalcohol (alditol) has interesting applications in hygiene and nutraceutical formulations and products. Xylitol has the formula \((\text{CHOH})_3(\text{CH}_2\text{OH})_2\) and pentane – 1,2,3,4,5 –pentol. The structure of Xylitol is given below

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\begin{align*}
\text{H}_2\text{C} & \quad \text{OH} \\
\text{HC} & \quad \text{OH} \\
\text{HO} & \quad \text{CH} \\
\text{HC} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{OH}
\end{align*}
\]

In this study, the electrocatalytic activity and stability of chemically prepared carbon (C) and single walled carbon nanotubes (CNT) supported Pd and nanocomposite catalysts towards xylitol oxidation in alkaline, neutral and acidic medium were investigated. In addition, we have examined the influence of the concentrations of xylitol and the supporting electrolytes on the electrooxidation reactions.
4.2 EXPERIMENT

Vulcan carbon (VX 72), Single walled carbon nanotubes (CNT, Chengdu Organic Co. Limited, China), Xylitol, Palladium chloride (Sigma–Aldrich), xylitol (Sigma–Aldrich), sodium borohydride (Qualigens, India), sulphuric acid (Merck, India), sodium sulfate (Merck, India) and KOH (Merck, India) were purchased and used as received.

Pd was deposited on the C and CNT by the chemical reduction method. About 100 mg of C or CNT was dispersed in isopropanol and are appropriate amounts of (Pd–5 % wt i.e., 5 mg) PdCl₂ (5 mM) were added and stirred well. After 30 minutes, freshly prepared NaBH₄ solution was added drop wise into the above mixture. Then the mixture was stirred for another 30 minutes. The resultant product was separated by centrifugation at 3000 RPM and washed with isopropanol water mixture. The precipitate was dried at 110° C for 24 hrs. The preparation of modified electrode is described in previous chapter using Nafion as a binder.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Physical characterization of Pd/C and Pd/CNT nanocatalysts
Figure 4.1 Powder XRD profile for carbon supported palladium nanoparticles (----- C, ------Pd/C).

Figure 4.2 Powder XRD profile for Single walled carbon nanotubes supported palladium nanoparticles (----- C, ------Pd/CNT)
Figure 4.3 Transmission Electron Microscopic images of (b) Pd/C, (c) Pd/CNT

Figure 4.4 Energy dispersive X - ray spectrum of (a)Pd/C and (b) Pd/CNT
XRD patterns of Pd/C catalyst are shown in Figure 4.1. The diffraction peak at ca. 25° is due to the C (002) plane. In the pattern of Pd/C, the 2θ peaks at 38°, 44°, and 65° represent the Pd/C (100), Pd/C (200), and Pd/C (220) planes, respectively. Compared with pure Pd, there was a slight shift in diffraction peaks were observed. This was due to uniform mixing of Pd with C. For Pd/CNT catalyst a sharp peak at ca. 25° is due to the C (002) plane for CNT and which is having higher intensity than the pure Pd. The Pd peaks at 2θ at 40°, 48° and 65° confirms the formation of Pd/CNT nanocomposite. The elemental composition of the prepared nanocatalyst was analysed by EDS measurements by analysing the surface Pd nanoparticles present in the catalyst. In Pd/C the Pd nanoparticles of 4.8 % and Pd/CNT of 4.1 %. The difference due to the Pd nanoparticles embedded or present in the other part of the catalyst.

4.3.2 The Electrochemical behaviour of Pd/C and Pd/CNT modified electrode

The electrochemical behaviour of Pd/C and Pd/CNT modified electrode in neutral, acidic and alkaline medium was studied. Figure 4.6
shows the Pd/C electrode in neutral medium, it exhibits a strong oxidation peak at –0.25 V, due to the formation of Pd into PdO. While in the case of the Pd/CNT (Figure 4.7) electrode the higher current density was observed compared with Pd/C and the reduction of PdO to Pd was shown distinguishably at –0.29 V in the reverse scan. Figure 4.8 shows the electrochemical behaviour of Pd/C and Pd/CNT electrode in 1 M H₂SO₄. This exhibits two strong peak at +0.4 V and +0.7 V, indicates the formation of PdO and during the reverse scan a strong reduction peak at +0.45 V was also observed. Both electrodes exhibit a similar electrochemical behaviour except the peak current density and exhibits similar activity in both alkaline and acidic medium. In alkaline medium the hydrogen adsorption region was high in both Pd/C and Pd/CNT electrodes. The oxidation of Pd to PdO was also exhibited in more positive potential and the reduction of PdO to Pd shows at -0.4 V (Pd/C) & +0.48 V (Pd/CNT). Generally the Pd exhibits better electrocatalytic activity in alkaline medium when compared to acidic and neutral medium. Hence the detailed investigation in alkaline medium was performed.

Figure 4.9 shows the first CV recorded for a Pd/C electrode in 1 M KOH solution. During the first cycle, as soon as the forward scanning is started from –1.1 V, a strong oxidation peak was observed at –0.6 V. It indicates that the oxidation of Pd-OH_ads to PdO. In subsequent cycle, especially in the fourth cycle the hydrogen adsorption peak was observed and at the same time the reduction peak of PdO to Pd was shown clearly at -0.38 V. Pd/CNT electrode exhibits similar electrochemical activity like Pd/C electrode. The hydrogen adsorption, oxidation and reduction of Pd peaks were clearly shown in the Figure 4.9. In the fourth cycle a slight shift in hydrogen adsorption was observed. Reduction potential of PdO to Pd is also shifted to the lower region (negative potential) for Pd/CNT electrode compared to Pd/C electrode. The ESA for Pd/C and Pd/CNT is 148 and 246 c g⁻¹ respectively.
Figure 4.6 CV of Pd/C in 1M Na$_2$SO$_4$ solution

Figure 4.7 CV of Pd/CNT in 1M Na$_2$SO$_4$ solution
Figure 4.8 CVs of (a) Pd/C and (b) Pd/CNT in 1 M H$_2$SO$_4$ solution

Figure 4.9 CVs of (a) Pd/C and (b) Pd/CNT in 1M KOH solution
Figure 4.10 CVs of Pd/C in (a) 1\textsuperscript{st} and (b) 4\textsuperscript{th} cycle in 1M KOH solution

Figure 4.11 CVs of Pd/CNT in (a) 1\textsuperscript{st} and (b) 4\textsuperscript{th} cycle in 1M KOH solution
4.3.3 Electrooxidation of Xylitol at Pd/C and Pd/CNT modified electrode

The electrooxidation of Xylitol (Xyl) was studied at Pd/C and Pd/CNT electrodes in 1 M Na$_2$SO$_4$/0.1 M Xyl solution. Figure 4.12 shows the electrooxidation of Pd/C and it exhibits an anodic oxidation peak at +0.505 V with peak current density of 36 mA/cm$^2$. The electrooxidation of Xyl does not show any oxidation peak in reverse scan. But a strong reduction peak of PdO to Pd was observed at +0.19 V with the peak current density of 19 mA/cm$^2$. In Pd/CNT electrode, the oxidation peak of Xyl exhibits a hump like curve at +0.7 V with the peak current density of 300 mA/cm$^2$ and no oxidation peak were observed in the reverse scan. But a strong reduction peak for the reduction of PdO to Pd was observed at +0.18 V.

![Figure 4.12 CVs of the electrooxidation of Xylitol at (a) Pd/C and (b) Pd/CNT in 1 M Na$_2$SO$_4$/0.1 M Xyl solution](image.png)
Figure 4.13 CVs of the electrooxidation of Xylitol at (a) Pd/C and (b) Pd/CNT in 1 M H₂SO₄/0.1 M Xyl solution

Figure 4.14 CVs of electrooxidation of Xylitol at (a) Pd/C and (b) Pd/CNT in 1 M KOH/0.1 M Xyl solution
Figure 4.15  CVs of the electrooxidation of Xylitol at Pd/CNT in (a) 0.1 M KOH/0.1M Xyl, (b) 0.5 M KOH/0.1M Xyl and (c) 1 M KOH/0.1M Xyl solution

Figure 4.16  CVs of the electrooxidation of Xylitol at Pd/CNT in 1 M KOH/0.1M Xyl solution in the scanning potential (a) -1.1 to +0.2 V and (b)-1.1 to +0.4 V
Figure 4.17 Chronoamperometric studies of electrode stability for (a) Pd/C and (b) Pd/CNT at 1 M KOH. 0.1 M Xyl solution.

Figure 4.13 exhibits Xyl electrooxidation in acidic medium at Pd/C electrode at +0.7V and reduction of PdO to Pd was observed at +0.48V. Both the electrodes show similar electrocatalytic activity with the high peak current density for Pd/CNT compared to Pd/C electrode.

Generally Pd shows better electrocatalytic activity in the alkaline medium (Antonlini et al 2009). The electrooxidation of Xyl was studied in the alkaline solution i.e., KOH solution and shown in Figure 4.14. Figure 4.14a shows the electrooxidation of Xyl at Pd/C electrode, and it exhibits an anodic oxidation peak vertex at -0.18V with the peak current density of 591mA/cm$^2$. A strong oxidation of intermediates formed during the forward scan was observed in -0.35V with the current density of 484 mA/cm$^2$. 

![Graph showing current density vs time for Pd/C and Pd/CNT electrodes.]
The Pd/CNT electrode shows an anodic oxidation at -0.009 V and an oxidation peak during reverse scan observed at -0.33 V. The $I_p/I_b$ ratio for Pd/C and Pd/CNT electrode was about 1.4 and 1.46 respectively. This indicates that both electrodes exhibit a similar kind of activity. CNT based electrode exhibits higher peak current density i.e. almost three times higher peak current compared to carbon electrode and the peak potential was shifted in the positive direction at CNT electrode.

In order to evaluate the catalytic performance of Xyl various concentrations of Xyl in 1 M KOH was tested. The electrooxidation of Xyl in 0.1 M Xyl/1 M KOH exhibits higher peak current density compared to 0.5 M and 1 M Xyl in 1 M KOH. Which was due to the higher degree of dissociative adsorption of Xyl at Pd electrode. This facilitates the electrooxidation of Xyl. Hence, 0.1 M Xyl in 1 M KOH exhibits better current output.

The electrooxidation of Xyl was studied in the scanning potential of –1.1 to + 0.2 V and –1.1 to + 0.4 V as shown in Figure 4.16. It shows that while increasing the potential the peak potential in forward and reverse scan was shifted slightly and no marked difference in peak current density was observed. It indicates that the change in scanning potential does not show any appreciable change on the oxidation of Xylitol.
Figure 4.18  CVs of electrooxidation of Xyl on Pd/C modified electrode in 0.1 M Xyl/1M KOH at various scan rate [5 to 225 mV/s]; Inset: calibration plot for EG electrooxidation peak current density vs. square root of scan rate

Figure 4.19  Long–term stability of Pd/C and Pd/CNT electrode in 1 M KOH/0.1M Xyl solution
The stability of Pd/C and Pd/CNT electrode was studied by the chronoamperometric method in 0.1 M Xyl/1 M KOH (Figure 4.17). The Pd/CNT electrode shows higher stability compared to Pd/C towards Xyl electrooxidation. The electrode stability was further studied by varying the scan rate in the Xyl electrooxidation reaction (Figure 4.18). The peak current density against the square root of scan rate reveals that the electrode is highly diffusion controlled one (r=0.992). The long term stability of Pd/C and Pd/CNT electrodes were tested up to 500 cycles, the current densities were decreased by 7% (Pd/CNT) and 5-6 % (Pd/C) (Figure 4.19).

4.4 CONCLUSION

The CV response of Pd/C and Pd/CNT catalysts during xylitol electrooxidation shows great differences in alkaline, neutral and acidic solutions. The concentration of Xyl and the supporting electrolytes also affects the electrooxidation reaction. High electrocatalytic activity and stability are observed in alkaline solution. The concentration of potassium hydroxide affects the oxidation peak on both potential and current density, and a higher alkalinity is favourable to the reaction. An oxidation peak at a higher potential with a significant current was declined in neutral solution. A further positive shift in peak potential was observed in acidic solution. The electrochemical response for Xyl at KOH was almost similar to both these electrodes. CNT support displays higher current response compared to C support.