
Synopsis

Availability of appropriate forms of energy is one of the basic needs of the society. The demand for worldwide energy has been increasing, while the conventional energy sources have been depleting fast. As the present main sources are fossil fuels, environmental pollution and its consequences caused by emission from combustion of them has also been a social concern. Thus, exploration of alternate energy sources has become an important area of research and development. Fuel cells are considered to meet a variety of applications. A direct liquid fuel cell (DLFC), which employs a liquid consisting of small organic compound such as methanol as the fuel, is more interesting than the other kinds of fuel cells. In view of this, studies on electrooxidation of organic compounds are important. A suitable catalyst plays an important role on the kinetics of electrooxidation of these compounds. The catalyst needs to exhibit a high activity, economical and stable over a long duration of its use. The catalysts, essentially noble metal-based materials, are usually dispersed on conducting supports such as carbon powder. Conducting polymers are also important for the application of supporting catalysts in view of their high conductivity, ease of preparation and chemical stability. Poly(3,4-ethylenedioxythiophene) (PEDOT) is known to be superior to other conducting polymer such as polyaniline, in the above properties. In the studies described in this thesis, several catalysts in nanodimensions are electrochemically deposited on PEDOT, which is also prepared electrochemically on carbon paper current collectors. Electrooxidation of a few organic compounds is studied and the positive influence of PEDOT is demonstrated. The contents of the thesis are briefly given below.

Chapter 1 provides introduction to electrocatalysis with a focus on factors affecting the electrocatalysis, different types of electrocatalysts and supports for catalyst and applications of PEDOT. This chapter also provides aim for various studies performed and presented in the thesis. Experimental details are reported in Chapter 2.

Studies on electrooxidation of formic acid on nanoparticles of Pt electrodeposited on PEDOT/C electrode are reported in Chapter 3. The most promising electrocatalyst for formic acid oxidation is Pt. Because Pt based catalysts are expensive, achieving the highest possible catalytic activity from a minimum loading of Pt is a challenging task.

Nanoparticles of Pt are electrochemically deposited on PEDOT, which is also electrochemically deposited on carbon paper substrate. A thin layer of PEDOT on carbon paper substrate facilitates the formation of uniform, well-dispersed nanoparticles of Pt, when compared with Pt deposition on a bare carbon paper substrate. TEM studies suggest that the nanoclusters of about 50 nm consist of nanoparticles of about 5 nm in diameter. Dispersion of fine Pt particles on PEDOT is expected to minimize or optimize the loading level of the catalyst. The voltammetry studies suggest that peak current for formic acid oxidation are several times greater on Pt-PEDOT/C electrode than Pt/C electrode. The catalytic activity and CO tolerance of Pt-PEDOT/C electrodes for electrooxidation of formic acid is significantly greater than that of Pt/C electrodes. Results of these studies are described in Chapter 3.

Comparison studies for electrooxidation of C₁, C₂ and C₃ alcohols on nanodendritic Pd-PEDOT/C electrode are presented in Chapter 4 and 5. Polyhydric alcohols such as glycol, glycerol have also been investigated as the fuels for DLFCs due to their high boiling points and less toxicity than methanol. The faradic efficiency of polyhydric alcohols is also higher than that of methanol. Thus, electrooxidation of polyhydric alcohols are more interesting than the monohydric alcohols. In this present study, three dimensional tree-like Pd nanodendrites are formed on PEDOT coated carbon paper electrode by a controllable one-step electrodeposition method without the use of any template or additive. A thin layer of PEDOT on the carbon paper substrate facilitates the formation of Pd nanodendrites ranging from 500 nm to 6 μm (Fig. 1). In the absence of PEDOT under-layer, Pd deposition is smooth and non-dendritic. Both Pd-PEDOT/C and Pd/C electrodes are studied for electrooxidation of C₁, C₂ and C₃ aliphatic alcohols in an alkaline electrolyte. Owing to enhanced surface area and surface defects on dendritic Pd, the Pd-PEDOT/C electrode exhibits greater catalytic activity than the Pd/C electrode for oxidation of the three alcohols. Among them, glycerol exhibits a high rate of oxidation. Cyclic voltammetry studies suggest that peak current density increases with an increase in concentrations of alcohols and NaOH in the electrolyte. Cyclic voltammetry studies indicate that Pd-PEDOT/C electrode possesses a high electrochemical stability with greater catalytic activity than Pd/C electrode toward electrooxidation of alcohols. The amperometry and repeated cyclic voltammetry data suggest high stability of nanodendritic Pd in alkaline medium. Pd-PEDOT is expected to be an appropriate Pt-free electrocatalyst in alkaline fuel cells. Among all these alcohols, glycerol is expected to be

an appropriate alcohol for application as a fuel in alkaline fuel cells at nanodendritic Pd on PEDOT surface.

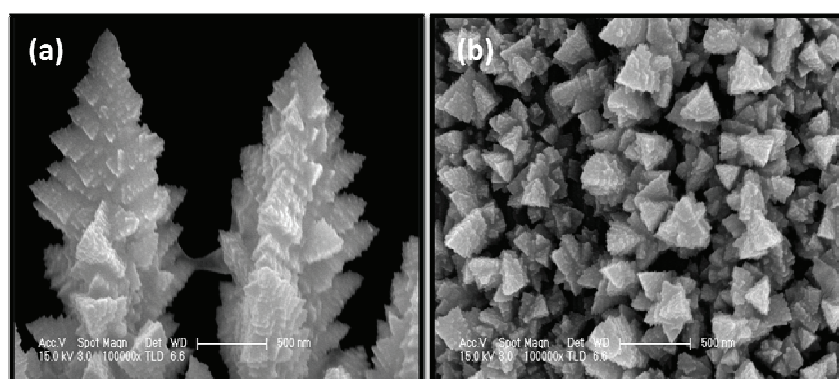


Fig. 1: SEM micrographs of (a) Pd-PEDOT/C and (b) Pd/C electrodes.

Studies on electrooxidation of glycerol on nanoflowers of PdRu deposited on PEDOT/C electrode are reported in Chapter 6. PEDOT supported PdRu catalysts with various Pd:Ru atomic ratios are prepared by one step electrodeposition method. The catalysts are characterised by a several techniques. X-ray diffraction (XRD) studies suggest that the nanoflowers of PdRu catalyst exists on PEDOT surface in an alloy form. X-ray photoelectron spectroscopy (XPS) results indicate a slight modification in electronic structure of Pd by alloying with Ru. SEM micrograph shows the 3D nanoflowers morphology of PdRu alloy on PEDOT/C surface. Ru alloyed with Pd significantly improves the catalytic activity for glycerol oxidation in comparison to Pd-PEDOT/C electrode. However, the activity for glycerol oxidation on pure Ru-PEDOT/C is not observed. Amongst all catalysts, Pd₅Ru nanoflowers on PEDOT surface exhibits highest electrocatalytic activity, real surface activity, exchange current density and stability (Fig. 2). Cyclic voltammetry and differential pulse voltammetry (DPV) are performed for analysis of glycerol. A series of voltammograms are recorded at Pd₅Ru-PEDOT/C electrode in the concentration range 1-20 mM glycerol in 1 M NaOH supporting electrolyte. Cyclic voltammetry determination of glycerol provides the detection limit of 10 μM . Under optimised conditions, significantly higher sensitivity and lower detection limit were obtained by differential pulse voltammetry (DPV) method in comparison with cyclic voltammetry method. DPV data indicates that Pd₅Ru on PEDOT is highly sensitive towards glycerol detection with sensitivity of $99.8 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ and low detection limit of $0.1 \mu\text{M}$. Thus, electrochemically deposited nanoflowers Pd₅Ru on PEDOT/C are efficient catalysts for direct glycerol oxidation as well as for analysis

purpose in alkaline media. The details of electrooxidation and analysis of glycerol are reported in Chapter 6.

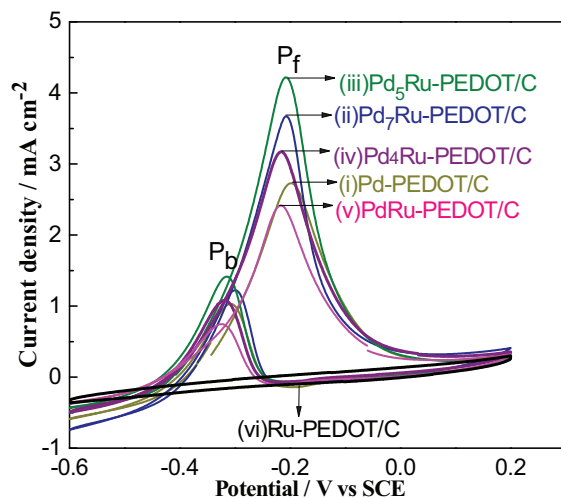


Fig. 2: Cyclic voltammograms of the Pd-PEDOT/C (i), Pd₇Ru-PEDOT/C (ii), Pd₅Ru-PEDOT/C (iii), Pd₄Ru-PEDOT/C (iv), PdRu-PEDOT/C (v) and Ru-PEDOT/C (vi) electrodes in 0.1 M glycerol + 1.0 M NaOH solution at a sweep rate of 5 mV s⁻¹. Current density is calculated on the basis of geometric area (1.4 cm²).

In Chapter 7, the effect of Pd decorated Au@Ag core shell on PEDOT surface for glycerol oxidation is investigated. In this study, nanodendrites of Ag are deposited on PEDOT/C surface by potentiostatic method. The nanodendrite of Ag-PEDOT/C electrode is used as a template for the synthesis of Au@Ag core shell via galvanic displacement reaction. The galvanic displacement of Ag with Au leads to the formation of Au@Ag core shell on PEDOT surface with different morphology by controlling the reaction time. The formation of Au@Ag core shell is confirmed by XRD, SEM, EDAX, TEM, HRTEM and XPS studies. XRD study exhibits that the epitaxial growth of Au on Ag surface. EDAX and XPS studies indicate that the atomic ratio of Au to Ag in Au@Ag-PEDOT/C electrode is tuneable by controlling the reaction time. Further to improve the activity of Au@Ag core shell is decorated with Pd by potentiostatic method. Different quantity of Pd deposition is carried out at different charges to optimize the activity of catalyst and it is found that the optimum charge for deposition is 0.25 C. The Ag-PEDOT/C electrode is electrochemically inactive for glycerol oxidation reaction. However, the addition of Au to Ag facilitates the oxidation reaction of glycerol. Electrocatalytic activities of Pd decorated Au@Ag-PEDOT/C electrodes for glycerol oxidation in alkaline medium are characterized by cyclic voltammetry experiments. A high catalytic activity of Pd-

(Au@Ag)-PEDOT/C(7.5 h) electrode with lower onset potential and higher current density is observed.

In Chapter 8, non-enzymatic oxidation and analysis of glucose is studied on Au nanoflowers surface. Glucose is abundant in nature, non-toxic, non-explosive, and non-volatile. The theoretical energy density of DGFCs is 4430 Wh kg^{-1} , which is estimated on the basis of complete oxidation of glucose to CO_2 releasing $24 e^-$ per glucose molecule. Therefore, it is attractive and appears to fulfil most of the requirement of a fuel for low temperature fuel cells. Au is potentiostatically deposited on PEDOT as well as carbon paper electrode. A layer of PEDOT on carbon paper substrate facilitates the formation of Au nanoflowers with an enhanced electrochemical active surface area, when compared with sub-micron size Au particles deposited on bare carbon paper electrode. Cyclic voltammetry of glucose is studied by varying the concentration of glucose, NaOH and sweep rate. Cyclic voltammetric peak current density increases with increase in concentrations of glucose and NaOH in the electrolyte. $^1\text{H-NMR}$ spectroscopy provides an evidence for oxidation of glucose to gluconic acid and formic acid. Repetitive cyclic voltammetry and amperometry studies suggest that the electrochemical stability of Au-PEDOT/C electrode is significantly higher than that of Au/C electrode. Au nanoflowers on PEDOT surface exhibit a high sensitivity value with low detection limit than that of Au/C electrode. Au-PEDOT/C electrode also exhibits a linear current response in glucose concentration ranging up to $10 \mu\text{M}$ with sensitivity of $515 \mu\text{A cm}^{-2} \mu\text{M}^{-1}$ (on the basis of geometric area) and a low detection limit of $0.03 \mu\text{M}$ with signal to noise ratio of 3. It is observed that uric acid and ascorbic acid do not show any significant interference effect on glucose analysis. Thus, electrochemically deposited nanostructured Au on PEDOT/C is an efficient catalyst for the direct glucose oxidation as well as for analysis purpose in alkaline media.

Electroanalysis of As(III) is studied on Pd-PEDOT/C electrode in an acidic medium and the details are reported in Chapter 9. Analysis of As(III) is interesting because it is important to remove As(III) in ground water. The Pd nanodendrites are grown on a porous thin film of PEDOT by electrodeposition process. The oxidation of As(0) at low concentration is characterized by an anodic peak at 0.20 V vs. standard calomel electrode (SCE). Cyclic voltammetry studies suggest that Pd-PEDOT/C electrodes exhibit greater electrocatalytic activity towards As(III)/As(0) redox reaction

than the Pd/C electrodes. Differential pulse anodic stripping voltammetry (DPASV) is performed for analysis of As(III) ion at pH 1.0 (Fig. 3(a)). The PEDOT modified Pd electrode is highly sensitive toward As(III) detection with sensitivity of $1482 \mu\text{A cm}^{-2} \mu\text{M}^{-1}$ (Fig. 3(b)). A wide detection range up to $10 \mu\text{M}$ and low detection limit of 7 nM (0.52 ppb) are obtained with a pre-deposition time of 120 s under optimum conditions. Interference effect of Cu(II) ions are investigated and it is observed that Cu(II) ions do not interfere. It is found that PEDOT does not have any influence on analysis of As(III).

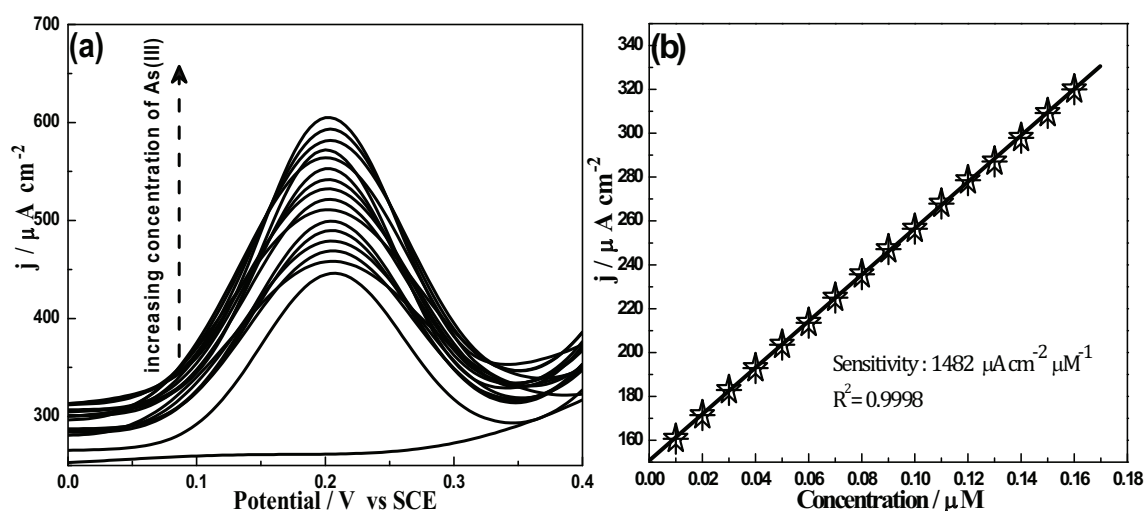


Fig. 3: (a) DPASV curves of Pd-PEDOT/C electrode in different concentration of As (III) + 1 M HCl and (b) DPASV calibration plots of Pd-PEDOT/C electrode peak current density versus arsenic concentration (pre-deposition at -0.30 V for 120 s). Current density (j) is calculated on the basis of geometric area (1.4 cm^2).

Details of the above studies are presented in the thesis. The work presented in the thesis is carried out by the candidate as a part of PhD training programme and most of the results have been published in the literature. A list of publications of the candidate is enclosed. It is hoped that the studies reported here will constitute contribution.