

The Electrochemical Atomic Layer Deposition of Pt and Pd Nanoparticles on Ni Foam for the Electro Oxidation of Alcohols

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Electrodeposition of Pt and Pd metal by surface limited redox replacement reactions was performed using the electrochemical atomic layer deposition. Carbon paper and Ni foam were used as substrates for metal deposition. Supported Pt and Pd electrodes were characterised using electrochemical methods and scanning electron microscopy (SEM). Cyclic voltammograms of the electrodeposited Pt and Pd on substrates showed features characteristic of polycrystalline Pt and Pd electrodes respectively. Ethanol oxidation in alkaline media was highly favoured on Pd/Ni foam than on Carbon paper while methanol oxidation was favoured more on Carbon paper than on Ni foam. Carbon paper and Ni foam produced good quality deposits and the EDX confirmed the presence of Pt and Pd particles.

Introduction

The future world energy mix requires introduction of new innovative alternative energy sources. To meet future global energy needs, electrocatalysts continue to be a very topical research area. Fuel cells continue to be investigated for possible tangible contribution to the energy mix. The high costs of PGMs need to be lowered for the direct alcohol fuel cells. This can be achieved by increasing Pt utilization and reducing the amount of Pt required in fuel cells [1]. The cost of the proton exchange membrane fuel cells (PEMFC) depends primarily on the costs of platinum and the membrane. The development of a new fabrication technique for membrane-electrode assembly (MEA), which will increase the Pt utilization, is one of the major issues in fuel cell research activities. There are three different electrode preparation methods that are commonly used. The first method involves the coating of the catalytic material on gas diffusion layer (GDL) and the second one is the decal transfer method. The third fabrication method is the direct coating of both sides of the membrane with the catalytic materials to form Catalyst Coated Membrane (CCM) and the combination of this structure with two GDLs. The MEAs fabricated with the decal method has a risk of uneven or incomplete transfer of catalyst from the transfer film to the membrane [1,2-4]. The catalytic layer can be applied on the membrane or GDL by different techniques, namely: rolling, spray-coating, brush-painting and printing methods [5] followed by drying and hot pressing. In this report, Electrochemical Atomic Layer Deposition (EC-ALD) was identified as a potential catalyst fabrication technique. EC-ALD is the electrochemical deposition method that involves alternated electrodeposition of atomic layers of elements on a substrate, employing under-potential deposition (UPD) in which one element deposits onto another element at a voltage prior to that necessary to deposit the element onto itself [6]. These deposition processes are typically carried out at ambient temperatures and use small concentrations of precursor

solutions (typically in millimolar levels). Different solutions are used to deposit each element separately. EC-ALD is an attractive technique because of the inherent advantages of sequential electrochemical deposition with self-limiting growth of deposits, features that may allow, for instance, fine-tuning of catalytic properties in relation to ratios of constituent elements, by way of stopping the growth of deposits at appropriate points. Khosravi et al. [7] coated the carbon paper with Au in order to perform Cu UPD for the deposition of Pt also aiming at reducing the Pt loading needed for FC. Whereas the fabrication of Pd on nanoporous gold film electrode was explained by Kiani et al. [8]. Mkwizu et al [9] demonstrated the synthesis of bimetallic multilayered nanostructures of platinum-based nanostructures involving Pt, Ru and Au using EC-ALD and derivatives of this layer-by-layer electrodeposition on model substrates with unique electrocatalytic properties for alcohol oxidation and oxygen reduction reactions in half-cell tests. The feasibility of catalyzing electrodic materials using the aforementioned method to generate platinum- and palladium-based catalysts on FC GDLs for MEA fabrication was explored and is reported herein.

Experimental procedure

The chemicals used in the preparation were Platinum solution (1mM H_2PtCl_6 pH = 1, SA Precious Metals), Pd solution (1mM PdCl_2 pH = 1, SA Precious Metals), (copper sulphate solution (1mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ pH = 1, Merck) were prepared in perchloric acid (0.1M HClO_4 , Merck). The chemicals were used as received without any further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 M Ω cm. The substrates used were carbon paper TGPH090 (PEMEAs) and Ni foam (Celmet, Japan: thickness = 1.6 mm, surface area = 7500 m²/m³, cell size = 0.5 mm, 48 – 52 cells per inch). Ni foam was cleaned in acetone, HCl and isopropanol followed by distilled water. Compressed air was used to dry the substrates.

The Cu UPD peak was not observed on the selected substrates (carbon paper and Ni foam) as shown in figure 1. Therefore the small Overpotential Deposition (OPD) voltage of -0.05V vs Ag/AgCl was used to deposit Cu on the substrates followed by the layer-by-layer electrodeposition of Pt and Pd as illustrated in figure 2.

Instrumentation

The automated experiments for the formation of Pt and Pd nanostructures were performed using custom-developed Lab-VIEW (National Instruments, TX) programs (virtual instruments) as described in [9]. The pumps, the five-way valve, and the potentiostat were all computer-controlled via standard RS-232 and USB interfaces. Four solutions could be independently delivered to the flow-cell via the outlet channel of the five-way valve. A vacuum pump was used to degas sample solutions prior to saturation with nitrogen. Nitrogen gas (99.99 %) was purged through the cell for 120 min before the measurements and this atmosphere was maintained throughout the experiments.

The three electrode flow cell at 25 °C was used for the electrochemical depositions. The flow cell was made up of two Perspex blocks for housing 0.84 cm thick Au wire and Ag/AgCl/3M KCl (BASF) as counter and reference electrodes respectively. The reference electrode was placed at the outlet channel of the cell. The substrate was used as the working electrode. The exposed area for deposition was 4.06 cm². Silicone rubber gaskets were used for sealing purposes (0.255 cm and 0.46 cm thickness). After assembling the cell, electrochemical cleaning was done in 0.1 M HClO_4 by applying 1 V potential for 5 minutes. The solutions were delivered by a sequenced cycle which

involved: (1) rinsing the cell with the background electrolyte (BE, 0.1M HClO₄), followed by filling the cell with 0.1 mM Cu²⁺ solution at selected applied potential E_{appl}, (2) Cu deposition at E_{ddep}, followed by rinsing the cell with the BE at E_{ddep}, (3) filling the cell with the 0.1 mM Pt⁴⁺ solution at open-circuit (OC), followed by the OC galvanic displacement reaction of Cu adlayers by Pt adlayers, followed by rinsing the cell with the BE at E_{ddep}. The step by step procedure for Pt deposition is summarized in Figure 1. 8x cycles for Pt deposition were used. The same procedure was followed for Pd deposition.

Characterisation of Pt and Pd nanostructures

The three electrode flow cell at 25 °C was used for the electrochemical activity studies by means of cyclic voltammetry. An AutoLab PGSTAT302 potentiostat was used for the studies. Au wire and Ag/AgCl/3M KCl (BASF) were used as counter and reference electrodes respectively. The Pt or Pd electrodeposited on the substrates (4.06 cm²) was used as the working electrode. CO stripping voltammograms were measured by the oxidation of pre-adsorbed CO (CO_{ads}) in 0.1 M HClO₄ solution at a scan rate of 50 mV/s. CO was purged into the 0.1 M HClO₄ solution for 30 min at 0.2 V vs Ag/AgCl electrode to allow the complete adsorption of CO. The excess CO in the electrolyte was purged out with N₂ for 50 min. For the alkaline medium, 0.1M KOH was used as the electrolyte. The scanning electron microscope (SEM) was used to observe the morphological structure and Energy dispersive X-Ray spectroscopy (EDX) with the accelerating voltage of 15 eV was used for estimating the bulk composition of the nanocatalysts.

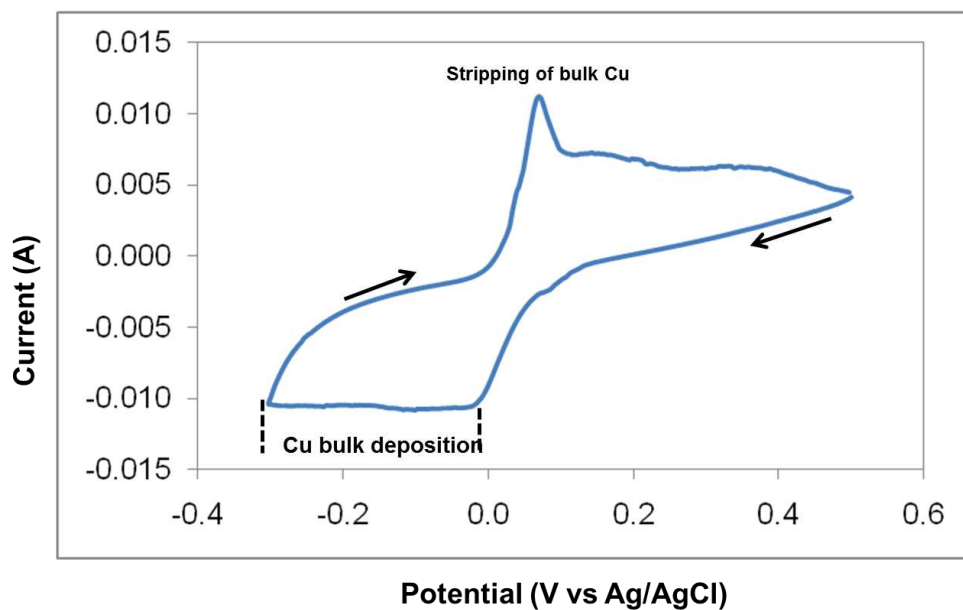


Figure 1. Cyclic Voltammogram for carbon paper in 0.1mM CuSO₄ + 0.1M HClO₄. Scan rate = 50 mV/s

Sequential electrodeposition coupled to Surface-limited Redox-replacement reactions: Synthesis of multilayered Pt electrocatalyst

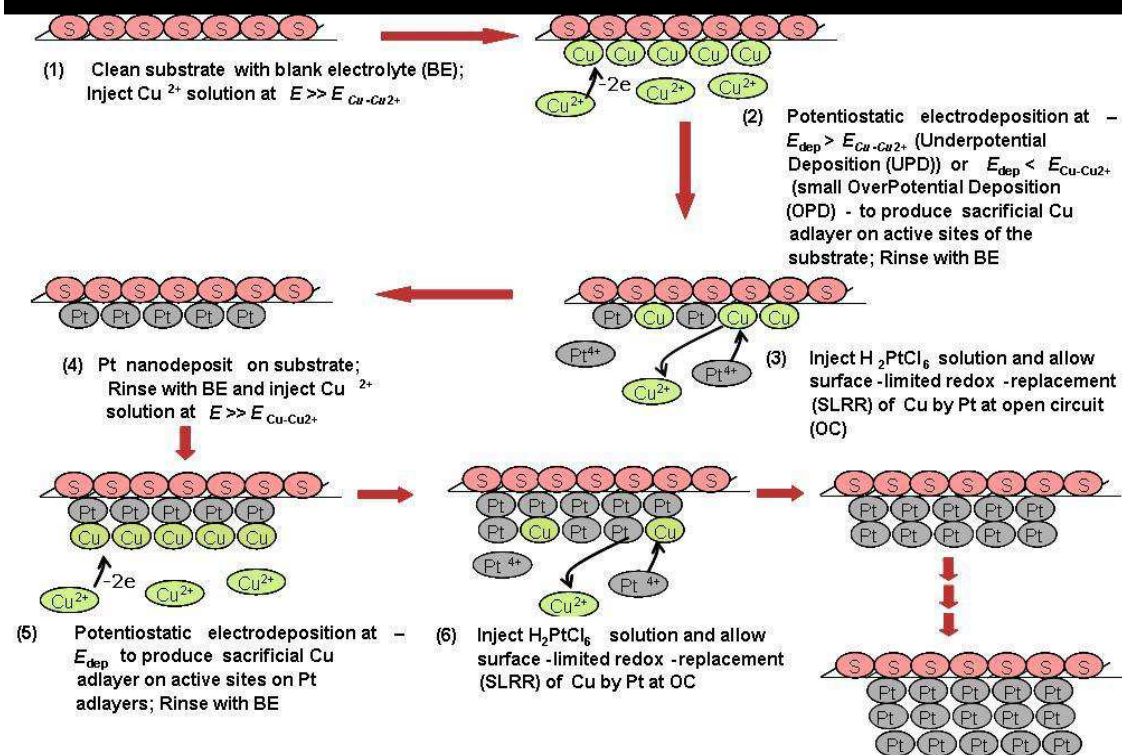


Figure 2. Sequential layer-by-layer electrodeposition of Pt using Cu as a sacrificial metal

Results and Discussions

Pt

The electrodeposited Pt on carbon paper and Ni foam showed activity towards methanol oxidation and CO adsorption in acidic medium as shown in figure 3 and figure 4 respectively. The onset potential for methanol oxidation on Pt/Ni foam shifted to lower potential than on Pt/Carbon paper. Hence Pt/Ni foam displayed better electrochemical activity than Pt/Carbon paper towards methanol oxidation.

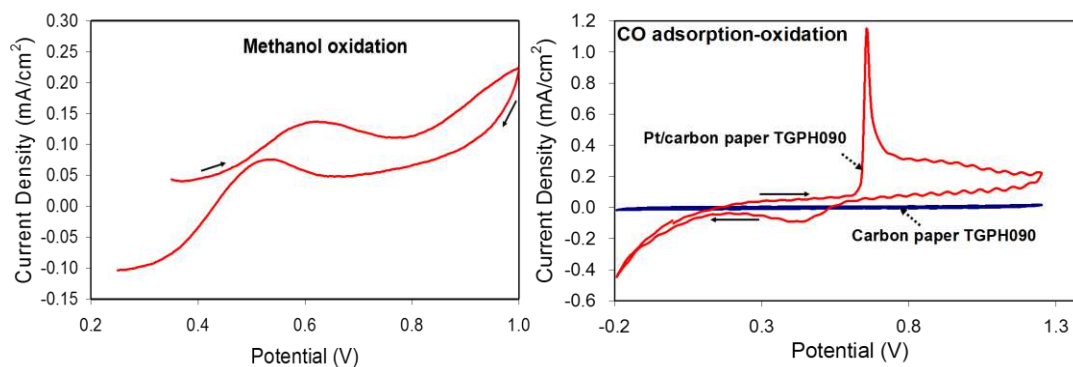


Figure 3. Cyclic Voltammograms of Pt on carbon paper in 0.1M Methanol + 0.1M HClO₄ and 0.1M HClO₄ + CO. Scan rate = 50mV/s

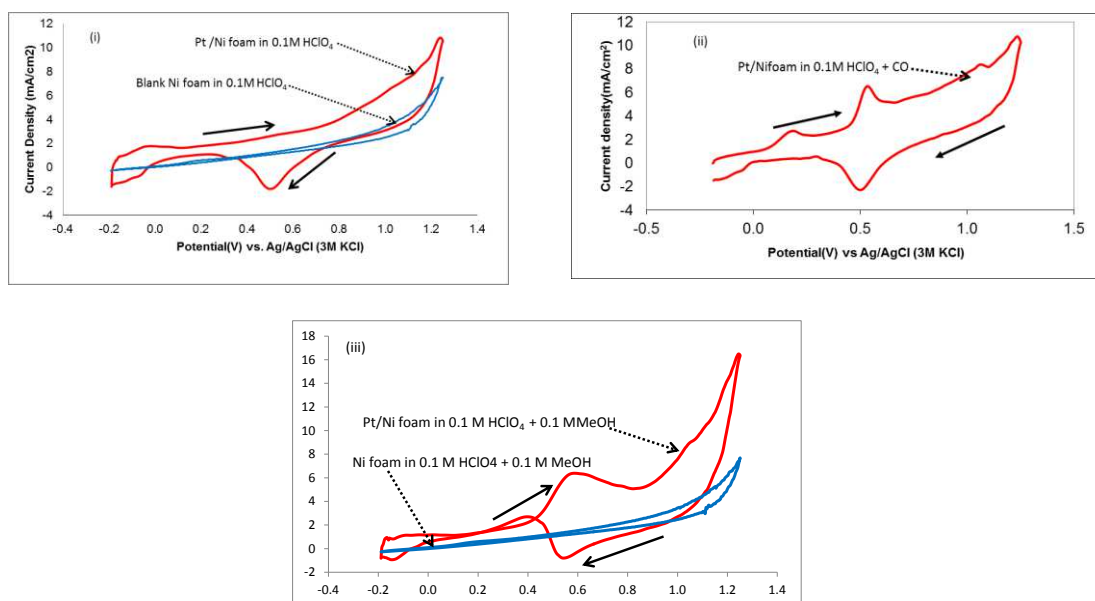


Figure 4. Cyclic Voltammograms of Pt on Ni foam in 0.1M Methanol + 0.1M HClO₄ and 0.1M HClO₄ + CO. Scan rate = 50mV/s

Figures 5 and 6 show the morphology of the Pt deposited on carbon paper and Ni foam respectively. The fibers of the carbon paper and Ni foam are uniformly covered with Pt particles. Agglomeration of Pt particles is observed at higher magnification on the carbon paper. EDX confirmed the presence of Pt on the substrates.

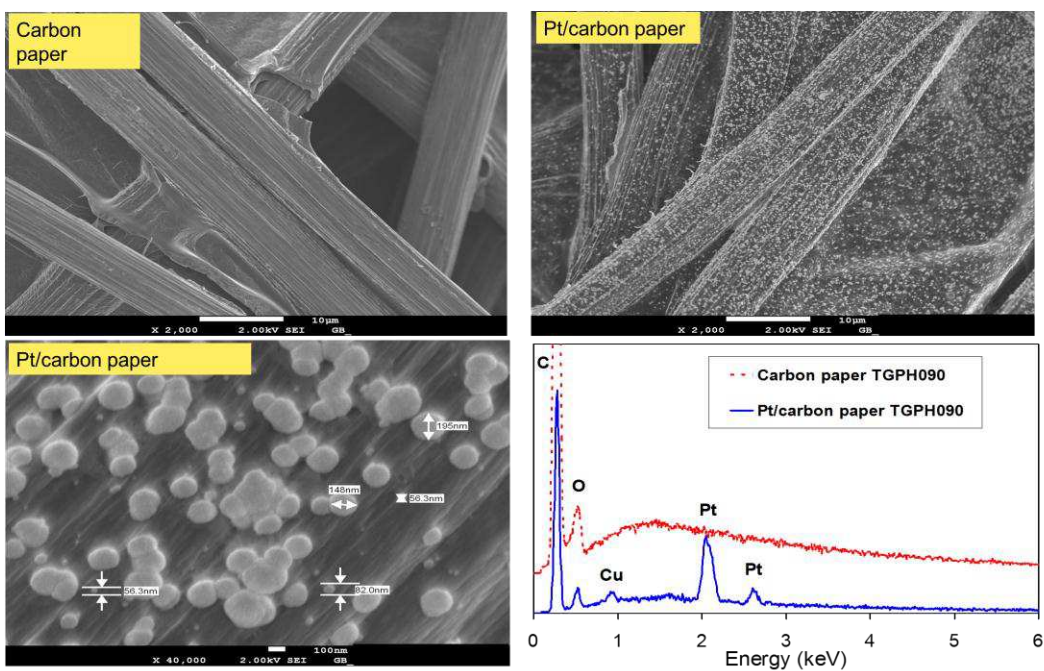


Figure 5. SEM micrographs and EDX profile of Pt on carbon paper

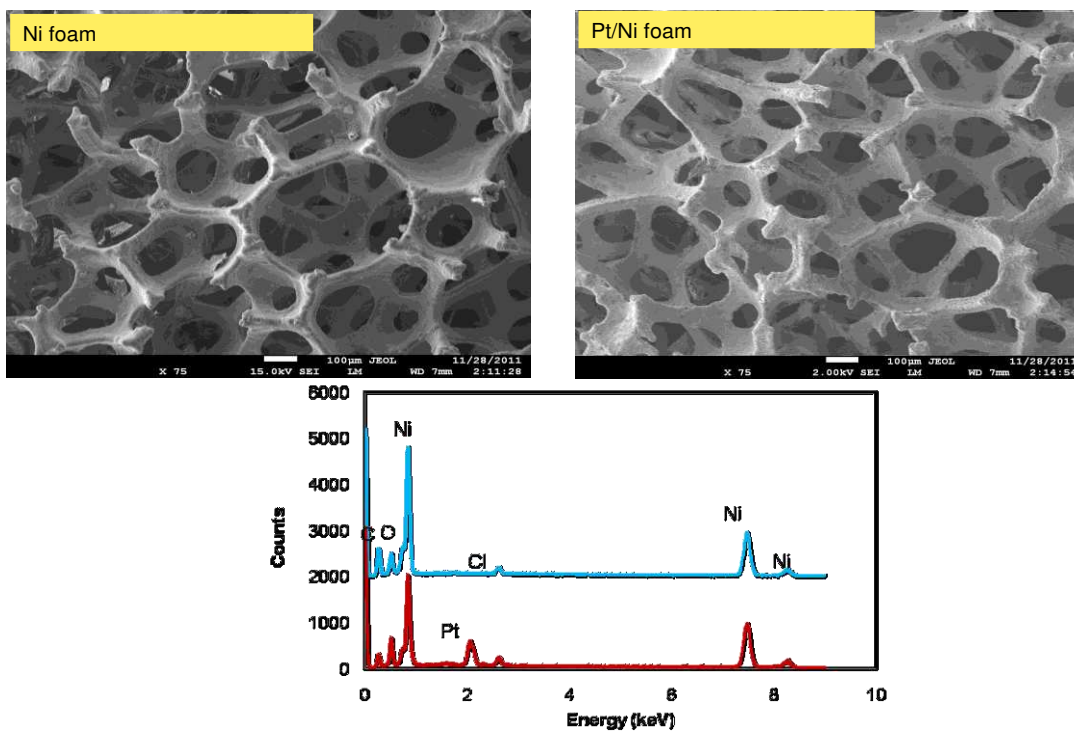


Figure 6. SEM micrographs and EDX profile of Pt on Ni foam

Pd

Pd deposited on carbon paper and Ni foam showed features characteristic of polycrystalline Pd electrode in acidic electrolyte as observed in figure 7. The Pd-based particles were not active towards alcohol oxidation in acid medium and this agrees with literature [10]. The activity of Pd-based catalysts was detected in alkaline medium as illustrated in figures 8 and 9.

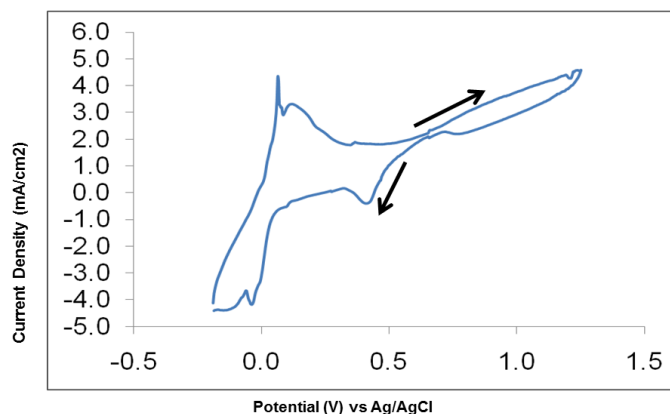


Figure 7. Cyclic Voltammograms of Pd on carbon paper in 0.1M HClO₄. Scan rate = 50mV/s

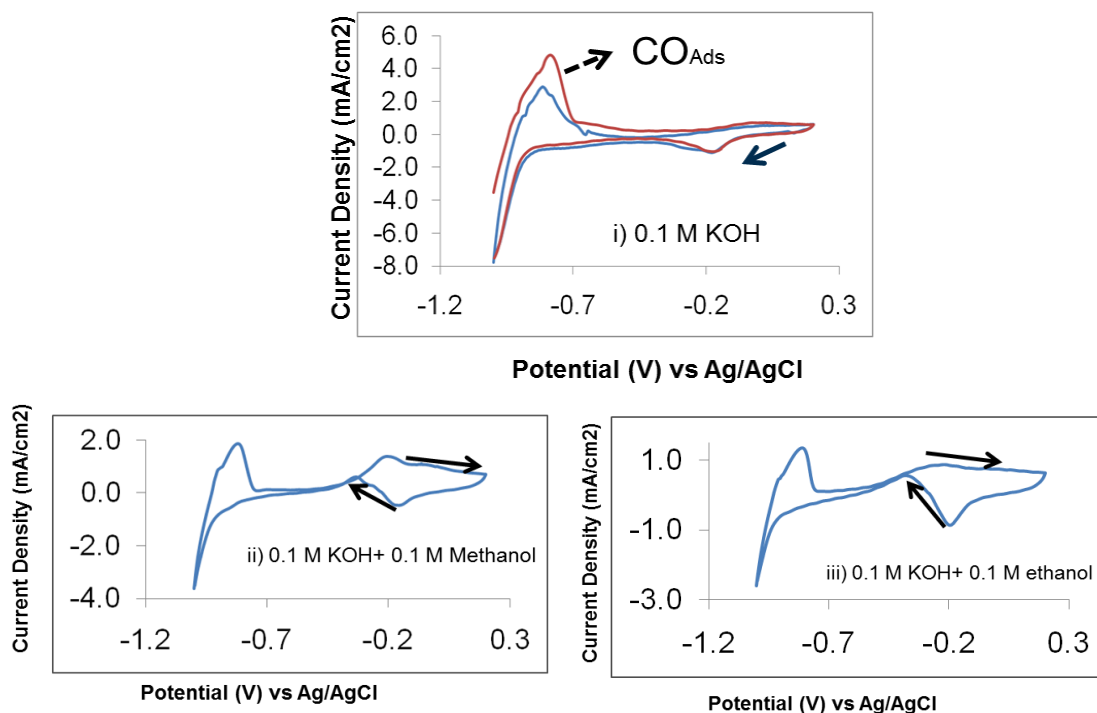


Figure 8. Cyclic Voltammograms of Pd on carbon paper in KOH. Scan rate = 50mV/s

The onset potential for methanol oxidation in alkaline medium on Pd/Carbon paper was more negative than on Pd/Ni foam implying better electrochemical activity.

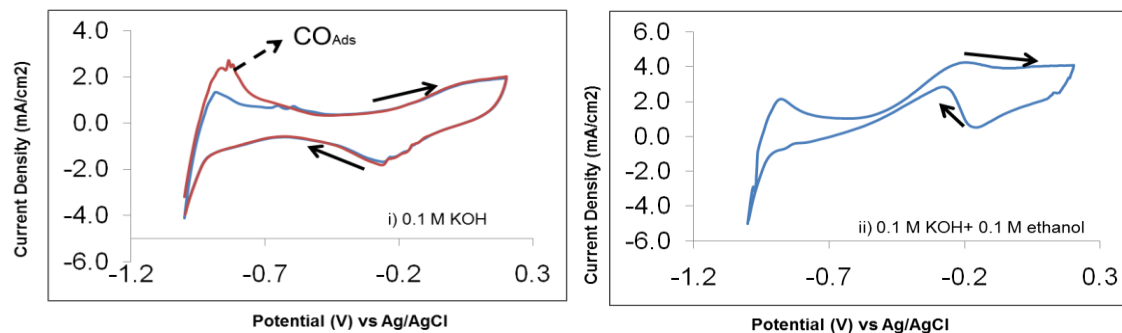


Figure 9. Cyclic Voltammograms of Pd on Ni foam in KOH. Scan rate = 50mV/s

Ethanol electrooxidation in alkaline electrolyte was enhanced on the surface of Pd/Ni foam than on Pd/Carbon paper. Both Pd/Ni foam and Pd/Carbon paper showed better capability against CO poisoning. Tables I and II give the summary of the electrocatalytic activity of the prepared catalysts.

TABLE I. Electrochemical Activity of Pt and Pd Towards the Oxidation of Methanol.

Catalyst	Onset potential (V vs Ag/AgCl)	If/Ib
Pt/Carbon paper	0.41	4.30
Pt/Ni foam	0.38	2.16
Pd/Carbon paper*	-0.456	2.86
Pd/Ni foam*	-0.429	1.30

*: methanol oxidation performed in alkaline medium

TABLE II. Electrochemical Activity of Pd Towards the Oxidation of Ethanol in alkaline electrolyte.

Catalyst	Onset potential (V vs Ag/AgCl)	If/Ib
Pd/Carbon paper	-0.555	1.58
Pd/Ni foam	-0.590	1.88

Figures 10 and 11 show the morphology of the Pd deposited on carbon paper and Ni foam respectively.

EDX confirmed the presence of Pd on both carbon paper and Ni foam.

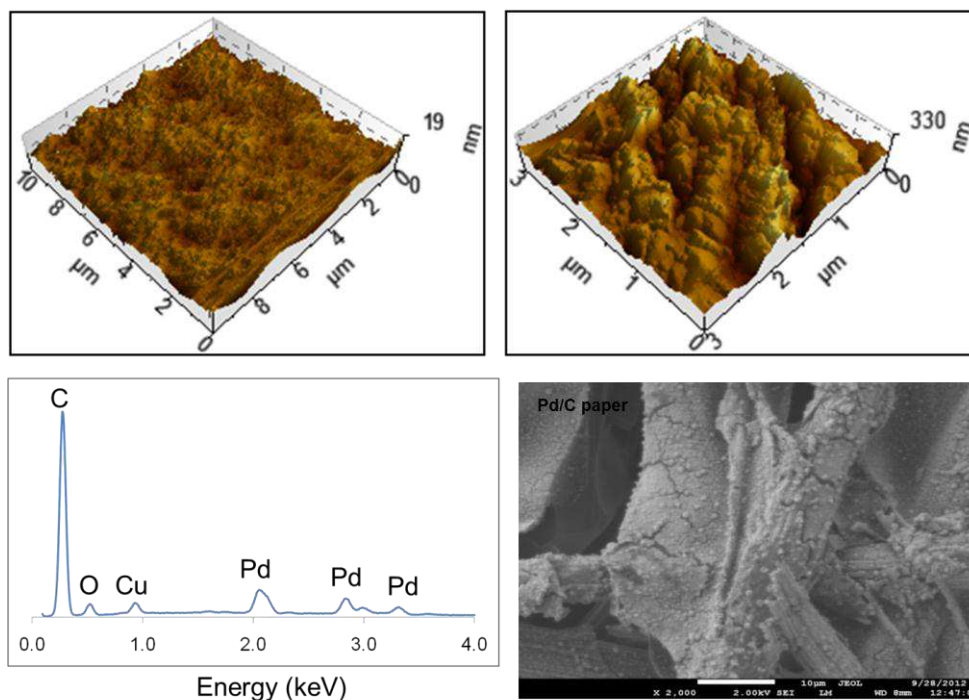


Figure 10. SEM and AFM micrographs as well as EDX profile of Pd on Carbon paper

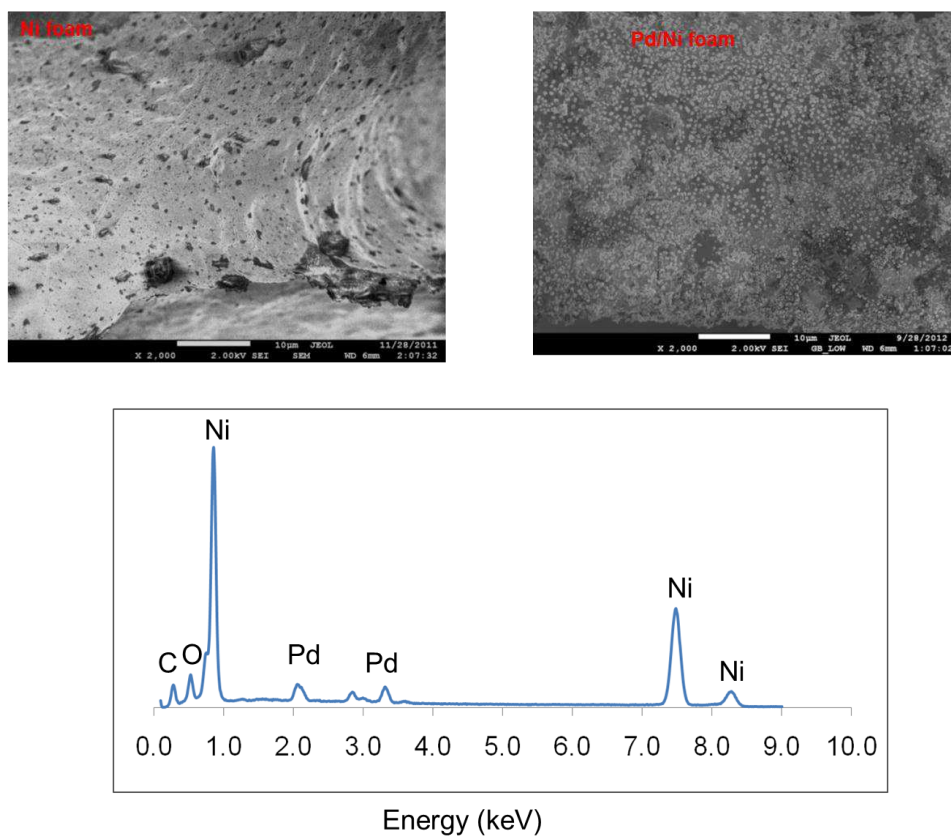


Figure 11. SEM micrographs and EDX profile of Pd on Ni foam

Conclusion and Future work

Pt and Pd were successfully deposited on carbon paper and Ni foam using ECALD technique. Cyclic voltammetric analysis of the electrodeposited Pt and Pd on the substrates showed voltammograms with features characteristic of polycrystalline platinum electrodes. In alkaline media Pd/Ni foam is a better electrocatalyst for ethanol oxidation than Pd supported on carbon paper while for methanol oxidation Pd/Carbon paper showed superior activity based on onset potentials. These electrocatalysts will be further characterized with inductive coupling plasma for elemental composition and AFM to determine the thickness of the catalyst coated substrate. The MEAs will be fabricated using the prepared electrocatalysts followed with ADAFC performance tests.

Acknowledgments

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