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Direct Electrodeposition of Graphene and Platinum Based Alloys-Analysis by SEM/EDX

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ABSTRACT

A novel, green and controllable approach was successfully made for the electrochemical synthesis of a composite coating made up from Electrochemically Reduced Graphene (ERGN) and Pt-based alloys using pulse power supply. The graphene were electrodeposited on carbon paper from graphite powder, anionic surfactant and sodium dodecyl sulfate which assists electrochemical exfoliation. Herein, Pt and PtCo were directly electrodeposited on graphene. The core-shell structured Cu/Pt, Ni/Pt, PdCu/Pt, NiW/Pt and FeNi/Pt alloys were prepared by a two-step method, in which the core Cu, Ni, PdCu, NiW and FeNi were first electrodeposited on the surface of the graphene. Shortly thereafter, one-step electrochemical displacement of Pt with core alloys electrodeposited on ERGN, was proposed to fabricate graphene-Pt based alloy coatings. This is the first report on electrochemical deposition/displacement of Pt based alloys on graphene and the coatings were characterized by HRSEM and the elemental analysis by EDX for the catalyst coated materials. The utilization of the platinum for efficient. Polymer Electrolyte Membrane (PEM) fuel cells was achieved by the use of graphene/carbon composites as catalyst support. The influences of the graphene/carbon support type on the fuel cell performance were analysed using Amrel electronic load.

Key words: Graphene, electrodeposition, Pt based alloys, carbon paper, galvanic displacement, fuel cells

INTRODUCTION

Recently, synthesis of nanoparticles of various metals, alloys and graphene play a vital role in engineering and applied sciences research as their inherent physical and chemical properties are superior than that of properties in bulk, which plays a crucial role in the development of energy devices like Proton Exchange Membrane (PEM) fuel cells, hydrogen storage (Nachimuthu *et al.*, 2014), batteries (Bae *et al.*, 2013) and sensors (Pumera *et al.*, 2010; Pumera, 2011).

Until recently, a wide spectrum of energy materials took part in the development of energy storage and applications, among them various nano materials with different nanostructures viz, nanorods, nanosheets, nanotubes, nanowires, composite and dendritic nanostructures, show an enhanced and efficient energy conversion with ultra low catalyst loading (Li *et al.*, 2013).

These novel energy materials can be synthesized via an electrochemical route with low cost, at ambient process temperature, high purity and with green nature. The electrochemical synthesis route has advanced much in applied science and engineering applications of nano energy materials with insitu structure property understandings (Li *et al.*, 2013), bimetallic deposition (Mkwizu *et al.*, 2010) and direct electro deposition of nano-composites (Tripathi *et al.*, 2013). The depletion of global energy is alarming for energy scarcity, in order to meet challenging energy exhausted and polluted environment, we are badly in need of environmentally friendly alternate energy resources. For effective utilization of renewable energy resources, it is required to develop electrochemical energy conversion and storage systems such as fuel cells, supercapacitors and batteries. Among them Fuel cells are efficient energy conversion and storage systems for today and future application. The need and necessity for nanostructured energy materials with high surface area for better performance of energy conversion devices can be achieved only with electrochemical synthesis route.

The other unique material which provides healthy and wealthy research platforms in the fields of chemistry, materials science and physics is graphene. Graphene is a mono atomic layer of carbon atoms sp^2 bonded into a two dimensional honeycomb structure and an allotropic form of carbon. Graphene is a fundamental building block of fullerence (0D), carbon nanotube (1D) and graphite (3D) (Geim and Novoselov, 2007). Graphene is a good supporting material for energy conversion and storage systems; as it has a good electrical conductivity and high surface area. Electrical conductivity is due to its electronic properties and extremely high carrier mobility (Geim and Novoselov, 2007). Due to its electronic property, it draws attention in applications of electrochemical energy conversion devices. An environment friendly, non polluting green energy electrochemical synthesis of graphene from pencil tip was reported (Singh *et al.*, 2012). Nowadays, it is well realized that the dispersion of metal nanoparticles on the graphene sheets also potentially provides a new way to develop novel energy materials.

The one pot electrochemical synthesis of graphene directly on carbon paper showed an excellent capability of electrodeposition and further modification of electrocatalysts embedded in a graphene support (Kakaei, 2012). Energy conversion devices require electro catalysts to be loaded with active conducting medium like graphene, which is a promising member of catalyst support. These supporting platforms increases the surface area of nano sized electrocatalyst for efficient electron transfer and mass transport of reactants to the electrocatalyst effectively (Li *et al.*, 2009; Kou *et al.*, 2009; Yoo *et al.*, 2009) and hence, a supporting material of metal free -carbon based has to be developed with high catalytic activity, long cycle stability, low poisoning effect and anode crossover (Gong *et al.*, 2009; Qu *et al.*, 2010).

Honma and co-workers (Yoo *et al.*, 2009) have experimentally found that Pt nanoparticles supported on graphene nanosheet (GNS) improved the performance of Methanol Oxidation Reaction (MOR) due to high surface area. Also, Electrochemically Reduced Graphene (ERGN) enhances methanol oxidation reaction for platinum catalyst (Kakaei, 2012). When comparing with Pt on activated carbon (Pt/C), the enhanced electrocatalytic activity of graphene supported Pt may be inferred to stronger interaction between flexible graphene sheets and Pt particles (Kakaei, 2012). Alloy nanoparticles usually show an increased electrocatalytic activity when compared to unalloyed nanoparticles (Guo *et al.*, 2010). Alloy, Pt-Ru/graphene showed an improved electrocatalytic activity than Pt/graphene (Dong *et al.*, 2010).

Core-shell nanostructures could be a promising strategy to reduce the catalyst costs due to the ultra low loading of noble catalyst but still maintain high catalytic reactivity. The high

surface-area-to-volume ratio of the core-shell nanoparticles would make the most efficient Oxygen Reduction Reaction (ORR) activity. The performance of a single cell with Cu/Pt core-shell structured catalysts show better performance for ORR. It is surprising that for a single Proton Exchange Membrane Fuel Cell (PEMFC) with output of power density 0.9 Wcm^{-2} using a very low Pt loading of 0.24 mg cm^{-2} at each electrode (Wei *et al.*, 2008). The Cu/Pt core-shell catalysts have potential and commercial viability for the fabrication of high performance electrodes in PEMFCs. Ni/Pt core shell nanoparticles synthesized via chemical reduction exhibited much enhanced catalytic activity towards ORR compared to the commercial E-TEK Pt catalyst (Wang *et al.*, 2010). However, there are still big rooms in energy conversion and storage systems for further developments in terms of efficient performance and scalable low-cost production. We hope this work can provide valuable awareness to researchers for gaining further understandings to speed up novel innovation in this area. There should be a commendable work ahead and no speed limit on the Graphene-way for new energy sources.

In this study, we have made a new attempt to synthesize alloy and core shell nano particles on Electrochemically Educated Graphene (ERGN) by electrochemical route.

The PEM fuel cells are eco-friendly power sources, which are essential for future energy solutions. They exhibit good energy efficiency and high power density per volume but the high costs of the noble metal catalysts, electrolyte membranes, bipolar plates and the control system limits considerable commercialization. The MEA-fabrication costs (Membrane Electrode Assemblies) can be reduced through increasing active surface area of catalyst by rising surface area of catalysts supports like graphene/carbon. In this work, due to some experimental difficulty only Pt on graphene alone was taken for PEM single cell performance hence, the work could be further extended to studying the catalytic activity of graphene based other Pt alloy catalysts for fuel cell performances.

MATERIALS AND METHODS

Preparation of graphene: Figure 1a shows schematics for the synthesis of graphene on carbon paper. Electrochemical reduction of graphene was performed with a carbon paper by an electroplating technique using Dynatronix (model: PMC10-20-60-PR Pulse power supply, Make: USA) by applying a constant DC potential of 6 V in an electrolyte solution containing graphite (Alfa Aesar) (5 mg mL^{-1}), Sodium Dodecyl Sulfate (SDS) (60 mM-Fischer scientific) accompanied by magnetic stirring for 60 min. Before electroplating graphene, the electrolyte solution was stirred at 55°C for 45 min. using temperature controlled magnetic stirrer with N_2 purging (Table 1).

To remove surfactant and capping materials on the surface of graphene, ERGN modified carbon paper is placed in acetone solution for 15 min and washed with plenty of deionized water (Kakaei, 2012). Shortly, after washing, the electrode was oven dried at 80°C to estimate loading of graphene by measuring weight differences between before and after plating (Table 2).

Deposition of PT, PtCo on ERGN: Figure 1b demonstrates electroplating of alloys on graphene coated carbon paper (ERGN).

Pt, PtCo were electrodeposited on the surface of ERGN modified carbon paper using plating bath composition and pulse parameters given in the Table 1 (Ayyadurai *et al.*, 2007), (Chaisubanan and Tantavichet, 2013). PtCo has received maximum attention as many fold increase in the activity for ORR has been demonstrated (Sarkar, 2009).

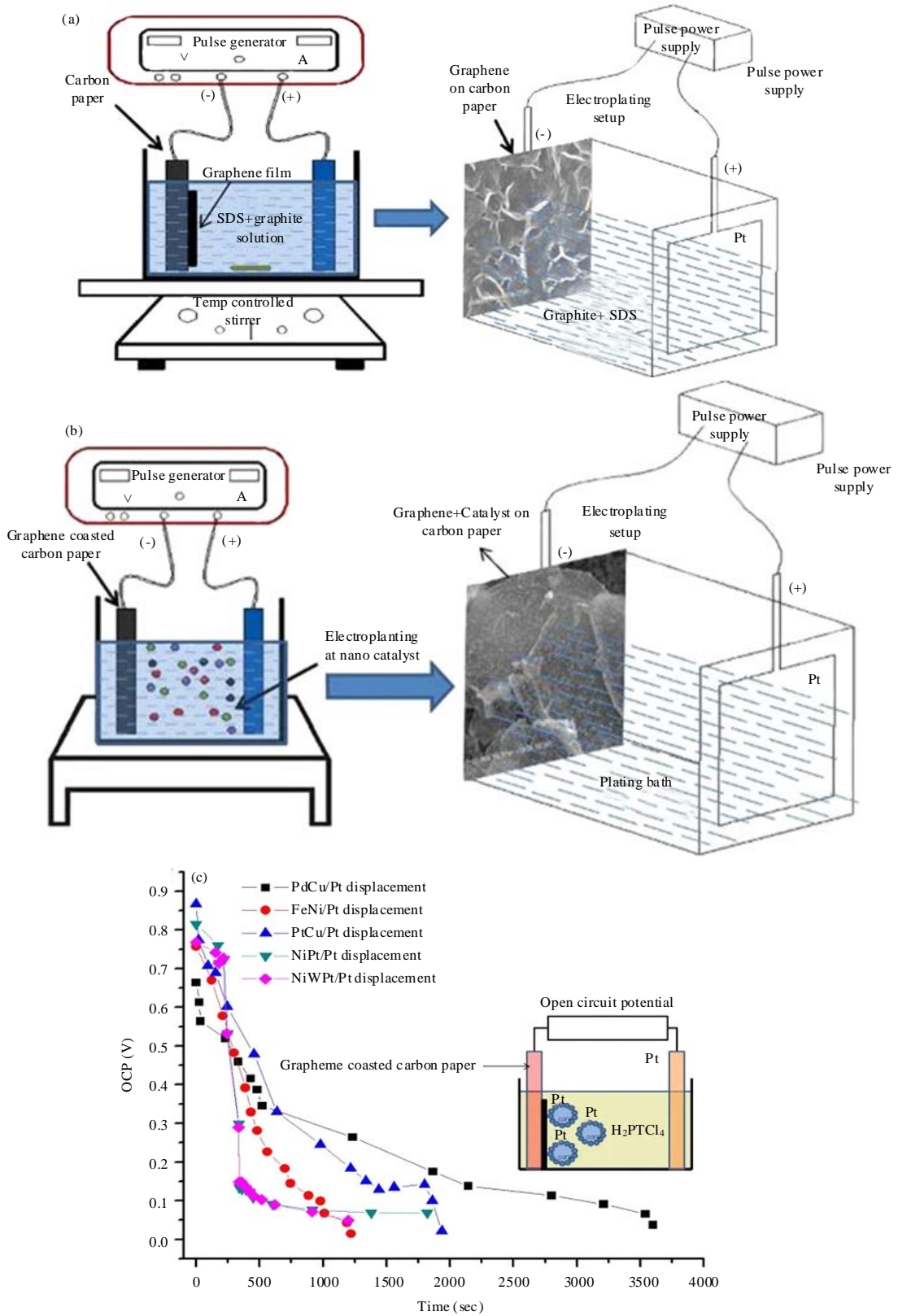


Fig. 1(a-e): Continue

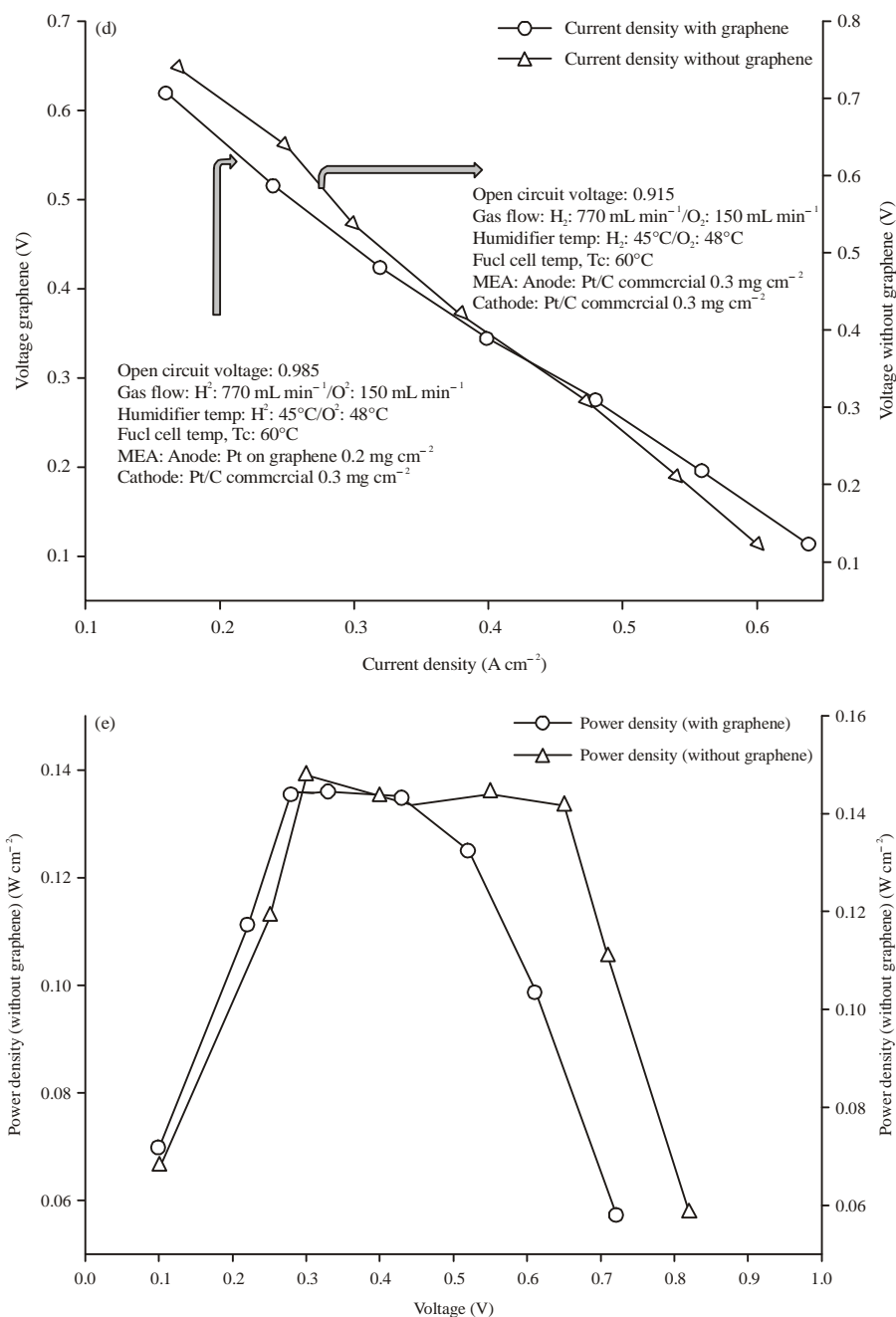


Fig. 1(a-e): (a) Schematic diagram of electrochemical synthesis of graphene, (b) Illustration diagram of electroplating of alloys on graphene coated carbon paper, (c) Open-Circuit Potential (OCP) of the electrode in contact with the $10\ g\ L^{-1}\ H_2PtCl_6$ displacement solution, (d) Cell voltage vs. current density and (e) Cell voltage vs. power density

A thin Pt or PtCo catalyst layer was deposited over the ERGN surface. After plating the catalysts, electrodes were washed with de-ionized water and oven dried at $80^\circ C$. The catalyst loadings were estimated from weight differences between before and after plating (Table 2).

Table 1: Pulse parameters and bath compositions of various alloys

Catalysts	Component	Contents (g L ⁻¹)	Pulses for EPa	Ipeak ^b A cm ⁻²	ATC ^c A.m ^d	Wetting agent for EP	Pt-displacement time (min)	Displacement solution	Content ^e (g L ⁻¹)	Ref ^f
Cu/Pt	CuSO ₄ .4H ₂ O	28	Total Time: 100 msec	1.25	0.15	IPA for 10 sec	32	H ₂ PtCl ₆ .6H ₂ O	10	Wei <i>et al.</i> (2008)
	(NH ₄) ₂ SO ₄	50	T _{on} : 1 msec T _{off} : 99 msec					HCl	60	
Ni/Pt	Na ₂ EDTA	42	Total Time: 109 msec	1	1.2	No wetting agent	30	TU (Thio Urea)	10 mg L ⁻¹	Hu <i>et al.</i> (2009)
	NiSO ₄ .7H ₂ O	20	T _{on} : 10 msec T _{off} : 99 msec					Do		
	C ₆ H ₅ KO ₇	25								
	Na ₂ CO ₃	24								
PdCu/Pt	NaCl	15.4	Total time: 100 msec	0.5	0.2	No wetting agent	60	Do		Vinogradov <i>et al.</i> (2001)
	NH ₄ Cl	26.8	T _{on} : 1 msec T _{off} : 99 msec							
	PdCl ₂	5								
	CuCl ₂ .2H ₂ O	1.5								
FeNi/Pt	Na ₂ EDTA	80	Total time: 109 msec	0.1	0.2	No wetting agent	20	Do		Li and Chan (2013)
	NH ₄ Cl	15	T _{on} : 10 msec T _{off} : 99 msec							
	NH ₄ OH	pH 9-9.2								
	FeSO ₄ .7H ₂ O	30								
NiW/Pt	NiSO ₄ .6H ₂ O	200	Total time: 109 msec	1.37	2.4	No wetting agent	20	Do		Lammel <i>et al.</i> (2012)
	H ₃ BO ₃	50	T _{on} : 10 msec T _{off} : 99 msec							
	Ascorbic acid	1								
	Na ₂ WO ₄ .2H ₂ O	20								
Pt-EP	C ₆ H ₅ KO ₇	25	Total time: 28 msec	0.45	1.2	No wetting agent	NA	NA		Ayyadurai <i>et al.</i> (2007)
	Na ₂ CO ₃	24	T _{on} : 3 msec T _{off} : 25 msec							
	NaCl	15.4	Total time: 109 msec	0.45	0.262	No wetting agent	NA	NA		Chaisubanan and Tantavichet (2013)
	NH ₄ Cl	26.8	T _{on} : 10 msec T _{off} : 99 msec							
PtCo-EP	H ₂ PtCl ₆ .6H ₂ O	10	DC: 6V	NA	Time: 60 min	No wetting agent	Na	NA		Kakaei (2012)
	HCl	60								
Graphene-EP	H ₂ PtCl ₆ .6H ₂ O	49.04								
	CoSO ₄ .7H ₂ O	28.11								
Sodium dodecyl sulfate	H ₂ SO ₄	49.01								
	Graphite powder	5								
	NaCl ₂ H ₂₅ SO ₄	17.30232								

^aEP: Electroplating, ^bIpeak: Peak current, ^cATC: Ampere time counter, ^dA.m: Ampere minutes e, g L⁻¹; Gram per litre, ^eRef: References, ^fEg: Cu/Pt; Coreshell, NA: Not applicable

Table 2: Estimation of loading for graphene and catalyst

Materials on carbon paper	Method of deposition	Graphene loading (mg cm ⁻²)	Effective catalyst loading (mg cm ⁻²)	Geometric area of coat (cm)
Graphene	Ep ^a	0.33	-	-
Pt	EP	0.33	3.67	1.50
PtCo	EP	0.33	0.20	1.20
Cu/Pt	EP-Cu/Pt-GD ^b	0.33	0.54	0.91
Ni/Pt	EP-Ni/Pt-GD	0.33	11.67	0.80
PdCu/Pt	EP-PdCu	0.33	0.67	0.90
NiW/Pt	EP-NiW/Pt-GD	0.33	9.27	1.26
FeNi/Pt	EP-FeNi/Pt-GD	0.33	5.87	0.52

^aElectroplating, ^bGalvanic displacement

In order to remove organic solvents and to reduce the oxidized catalysts, electrodes were heat treated at 250°C in H₂ atm for 2 h.

Formation of coreshell on ERGN

Electrodeposition of core materials (Cu, Ni, PdCu NiW and FeNi): The electrodeposition of core materials, Cu, Ni, PdCu, NiW and FeNi on ERGN was performed using ERGN as a working electrode and platinum foil as a counter electrode. Wetting agent Isopropyl alcohol (IPA) is used to increase wettability for homogenous deposition and to obtain reduced particle size for copper. The electrodeposition of Cu, Ni, NiW and FeNi to form a core, was deposited on the ERGN using a plating bath composition, pulse parameters given in Table 1.

Formation of Pt shell by displacement (of core materials): The Graphene on carbon paper (ERGN) electrodeposited with Cu particles was immersed immediately in a Pt displacement solution whose compositions (Wei *et al.*, 2008) given in Table 1, results formation of Pt/Cu coreshell particles by partial replacement of Cu with Pt. To eliminate the oxidation of Cu nanoparticles by dissolved oxygen, nitrogen was purged during the displacement. The displacement of copper by Pt was measured by the Open Circuit Potential (OCP) between working electrode and the counter platinum foil electrode. The OCP is reduced and approaches minimum value, which indicates that a majority of platinum in electrolyte, is deposited in working electrode (ERGN+core materials), as illustrated in Fig. 1c. The displacement time is measured externally and as shown in Table 1. In displacement bath, it is necessary to add Thiourea (TU) to prevent Cu dissolution by dissolved oxygen. To remove organic solvents and to reduce the oxidized catalysts, the electrode (Cu/Pt core shell on ERGN) was heat treated at 250°C in H₂ atm for 2 h. The illustration for galvanic displacement and core shell formation is depicted in Fig. 2.

Similarly, the other Ni/Pt, PdCu/Pt, NiW/Pt and FeNi/Pt core shell catalysts on ERGN were electrochemically synthesized.

RESULTS AND DISCUSSION

Electrodeposition: When compared to DC deposition, pulse electrodeposition results high concentration of metal ions in the vicinity of electrode surface will produce high current density. It offers efficient mass transfer kinetics by varying pulse parameters of on-time, off-time and peak current density. Also, a variation in pulse parameters shall form deposits of different morphologies (Choi *et al.*, 1998; Chandrasekar and Pushpavanam, 2008).

The potential and current are varied alternatively during electrodeposition. This is accomplished with equal amplitude pulses, time duration and polarity (Chandrasekar and Pushpavanam, 2008). In each pulse there is a periodic switching of current between on-time and off-time (no current) during plating of ionic particles on working electrode.

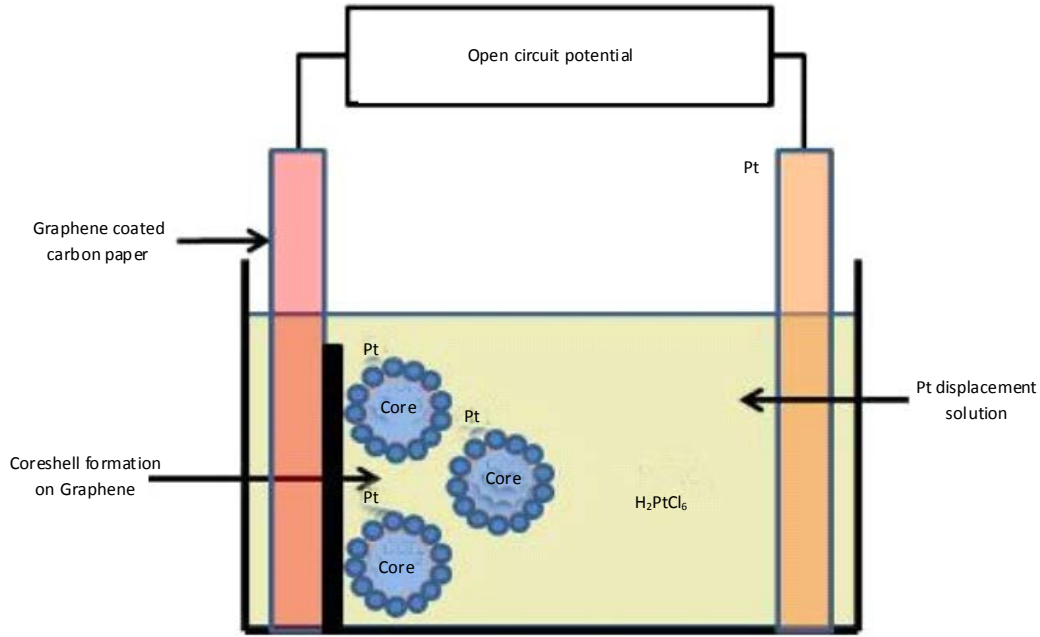


Fig. 2: Illustration diagram for displacement of Pt form outer shell of nano alloys on ERGN

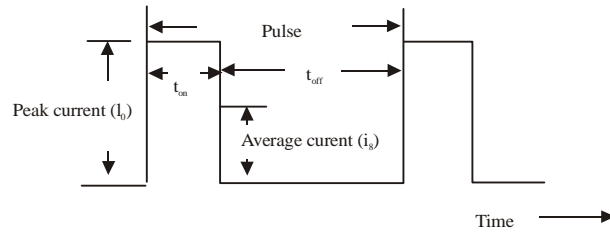


Fig. 3: Typical wave form of pulse current and deposition parameters

A typical pulse diagram is as shown in Fig. 3 (Karimi, 2011).

The basic pulse mathematics need to be known for understanding the terms involved in pulse cycle. In a pulsed current deposition, duty cycle (γ) is the total time of a cycle in percentage (Chandrasekar and Pushpavanam, 2008) and its reciprocal is frequency ($1/T$):

$$\text{Duty cycle} = \frac{T_{\text{on}}}{T_{\text{on}} + T_{\text{off}}} = T_{\text{on}} \times f$$

or:

$$\text{Frequency (f)} = \frac{1}{T_{\text{on}} + T_{\text{off}}} = \frac{1}{T}$$

The average current density (I_A) is defined as:

$$I_A = \text{Peak current } [I_p \times \text{Duty cycle } (\gamma)]$$

In Direct current plating, formation of negative charge cloud around the cathode will hinder the movement ions but in the case of pulse electrodeposition (PED), the charge cloud will get discharged and permits metal ions to migrate and to form a coating on working electrode. In electrolyte bath solution, there is scarcity of metal ions in peak current density areas when compared to low current density areas. In PED, metal ions were migrated to regions, where there is a lack of metal ions in bath during T_{off} . But the metal ions are densely formed and readily available for plating on electrode during T_{on} . Growth of new crystals on crystal lattice is generally influenced by the density of adatoms, high overpotential and lower surface diffusion rate which would be determined by pulse current (I_p). The I_p will increase the density of adatoms and nucleation rate during T_{on} . In PED, T_{on} determines fine grained microstructure. The distortions during T_{off} may result renucleation and which is due to the removal of impurities. At low Duty cycle, higher I_p is required for medium deposition rate. Hence, duty cycle is maintained as the minimal range of 33-50%.

There is a lack of uniform distribution of current at higher I_p during T_{on} irrespective of waveform employed during plating. T_{off} influences additive mass transfer in electrolyte and adsorption mechanism. For plating of alloys, usually high frequency pulses preferred for homogenous coating composition. By manipulating T_{on} and T_{off} , composition of alloy can be modified by producing multilayered deposits (Chandrasekar and Pushpavanam, 2008).

In this study, nano structured particles of metals/alloys were synthesized and deposited on the electrode with optimal pulse parameters discussed and experimented in the literature references (Table 1).

Ergn modified carbon paper: To coat graphene film on carbon paper, several experimental parameters including potential, temperature, concentrations of SDS, quantity of graphite, time of plating with and without using wetting agents, were optimized. Direct Electroplating of alloys was performed in constant current mode and electroplating of graphene in constant voltage mode.

Effect of electrodeposition parameters-ERGN: Firstly, the graphene film was electrodeposited onto carbon paper with different DC voltages from 3-8 V (constant voltage mode) and the uniform graphene coat was observed only at the potential of 6 V. The electroplating of graphene on carbon paper was experimenting at different heights from the level above stirring. At particular height, dispersion of graphite powders in electrolyte was uniform, which facilitates uniform electro coating of graphene on carbon paper. The efficiency of deposition of graphene layer on carbon paper were determined by current consumption during plating and values of average current, I_{av} , average voltage, V_{avg} displayed on the dynatronix. Electroplating time was allowed for 30 min to 1 h, at exactly 1 h duration, graphene was uniformly coated over the carbon paper surface of 5 cm² area.

At high bath temperature, electrolyte solution starts evaporating, leaving undispersed particles adsorbed on bath wall. When wetting agent, IPA is used, there was no graphene coating. Out of different concentrations of SDS from 14-60 mM, the Conc 60 mM found to be favorable for electro coating of graphene on carbon paper. The area of electro coating, loading of catalyst and graphene are summarized in Table 2.

Sem analysis

Graphene surface (ERGN): High Resolution Scanning Electron Microscopy (HRSEM) analysis of the graphene surface revealed the presence of graphene in the form of wrinkles (Fig. 4a).

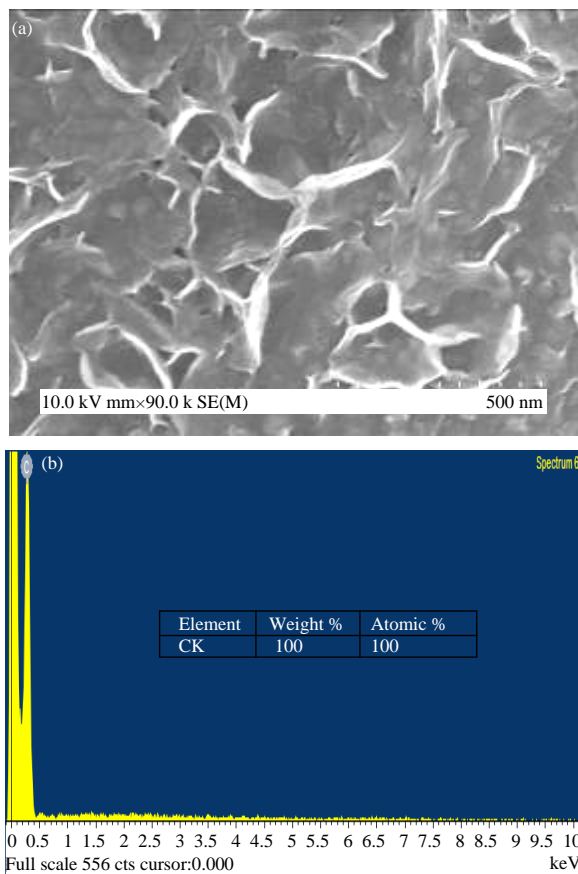


Fig. 4(a-b): (a) SEM image of electroplated Graphene on carbon paper and (b) EDX of electroplated graphene on carbon paper

The surface of the aggregated platelets is fairly uniform and a number of wrinkled structured graphene grown over surface of carbon paper. The presence of graphene as carbon is evidenced in Energy Dispersive X-ray (EDX) result as shown in Fig. 4b.

Pt on ERGN: Bright clusters are platinum on thin transparent graphene sheets (Fig. 5a). The average platinum particle diameter is around 30nm, which is considerably larger than desired. Figure 5b shows an SEM image of platinum nanoparticles on the graphene sheets. It is also possible that the particles visible in the SEM image actually aggregate of nano platinum particles. EDX (Fig. 5c) result shows the presence of Pt. Graphene supports the Pt catalyst layer consists of a dense and well defined roof particle structure as shown in Fig. 5b have taken part in finding fuel cell performances.

PtCo on ERGN: Figure 6a displays an SEM micrograph of PtCo on graphene. Image shows clusters of flower like structures on graphene sheets. The average PtCo particle diameter is around 60 nm and aggregated particles of size approximately 500 nm. Also shows a fine coating of PtCo on the graphene sheets which has dense PtCo nano particles on graphene sheets are recognizable at this magnification and EDX (Fig. 6b) analysis revealed the presence of PtCo nanoparticles.

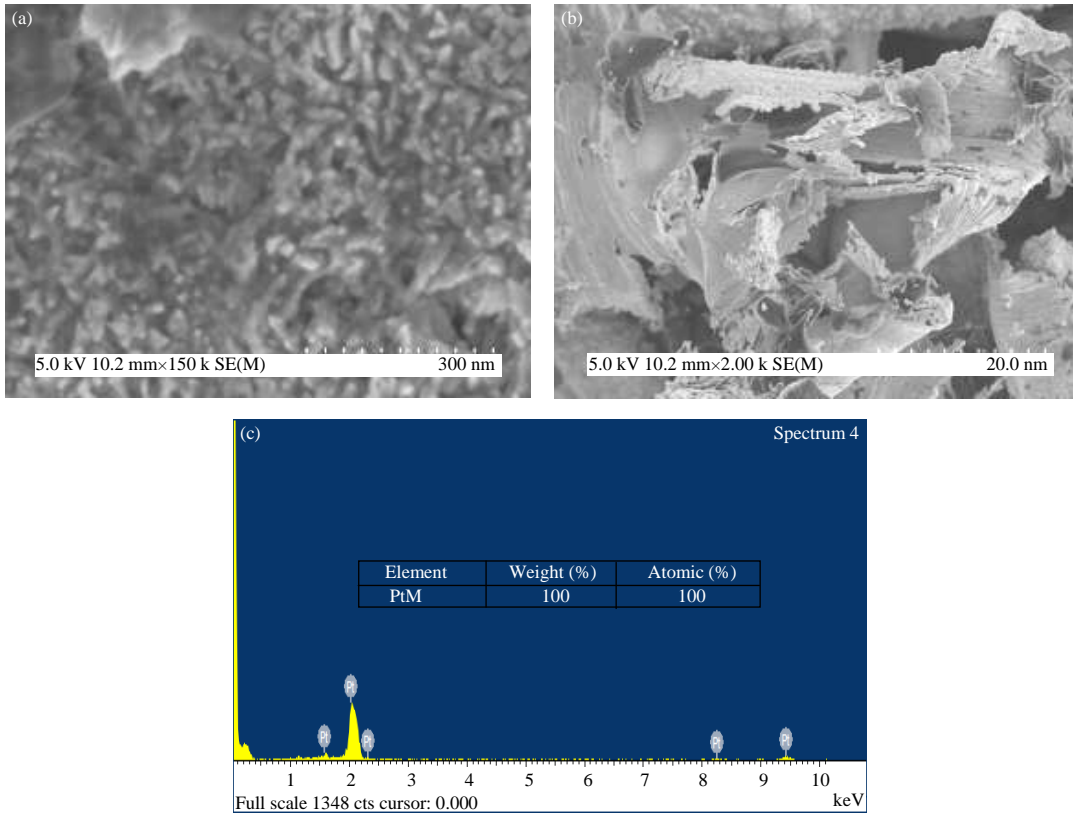


Fig. 5(a-c): (a-b) SEM image of Electrodeposited Pt on graphene at different magnifications and (c) EDX of Electrodeposited Pt on graphene

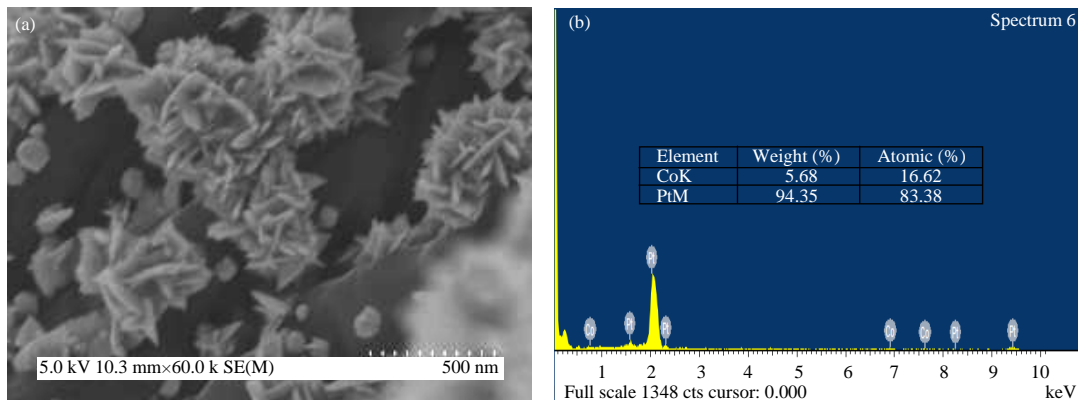


Fig. 6(a-b): (a) SEM image of electrodeposited PtCo on graphene and (b) EDX of electrodeposited PtCo on graphene

Cu/Pt coreshell formation on ERGN: Only a very few works were reported on the galvanic displacement of Cu by Pt metals, to form coreshell nanoalloys. For the displacement reaction to be

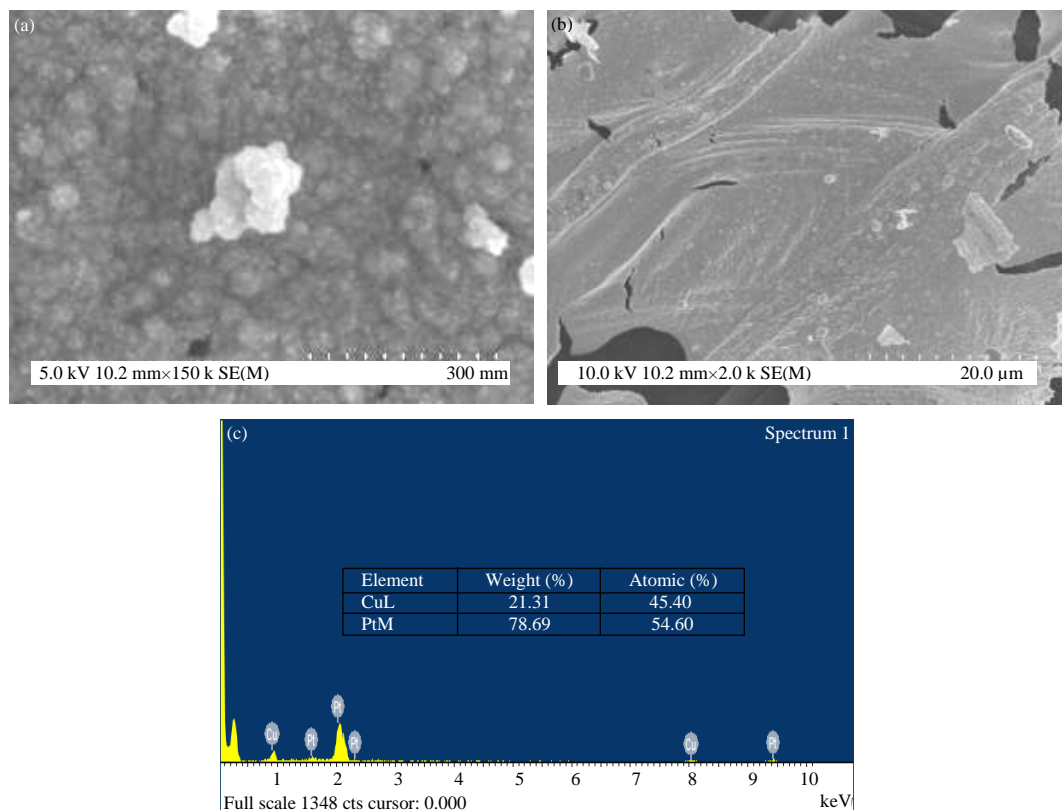


Fig. 7(a-c): (a-b) SEM image of Pt/Cu coreshell on graphene at different magnifications and (c) EDX of Pt/Cu coreshell on graphene

completed with satisfactory thermodynamics and kinetics, potential difference (E) between Pt (0.742 V vs Normal Hydrogen Electrode (NHE)) and Cu (0.340V vs NHE) is adequate. The difference in atomic radius values between Pt and Cu ($r_{Pt} = 1.39$ and $r_{Cu} = 1.28 \text{ \AA}$) shows that the galvanic displacement of Pt to form shell by Pt^{4+} on Cu core, results only a small amount of Pt atoms on the outermost surface of core Cu nanoparticles and hence layers below the surface of shells are available for subsequent chemical reaction (Sarkar, 2009). Finally, due to continuous chemical reaction, high pure Pt atoms are started forming on the outermost shell and a pure Cu on the inner core. This results with different weight percentages of Pt and Cu in Pt-Cu alloy, found in interface of pure Pt and pure Cu (Sarkar, 2009).

SEM analysis: Figure 7 shows clearly the presence of coreshell particles with graphene support. As can be seen from Fig. 7a. The catalyst particle size is about 40 nm is uniformly distributed on graphene. Figure 7b displays agglomerated coreshell particles at some areas on graphene. The brighter image particle shows platinum, which has a high atomic number compared to copper. The Cu/Pt core-shell nanoparticles have been confirmed by EDX (Fig. 7c) elemental analysis. Since, platinum and copper crystallites have the same crystal structure of face-centered cubic, it is easier to deposit Pt on the Cu surface than on any graphene or carbon support (Sarkar, 2009).

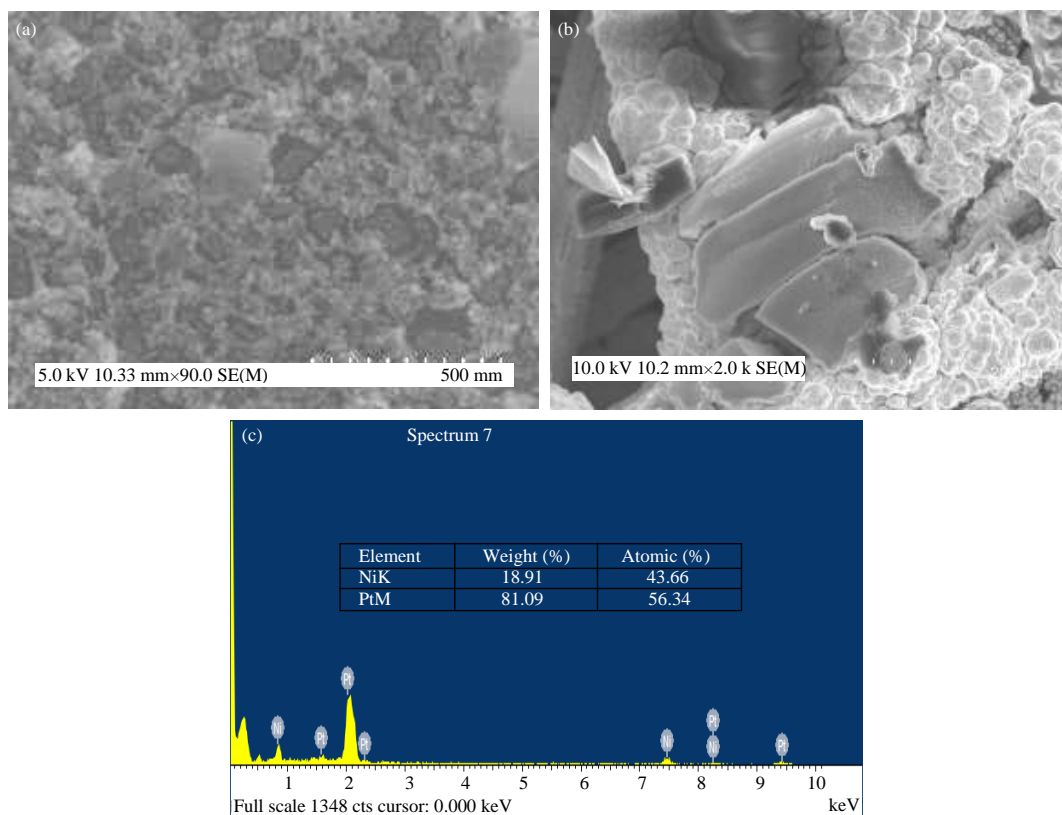


Fig. 8(a-c): (a-b) SEM image of Ni/Pt coreshell on graphene at different magnifications and (c) EDX of Ni/Pt coreshell on graphene

Ni/Pt coreshell formation on ERGN: The idea of displacing Pt particles with Ni particles were conceived by referring the work electrochemical synthesis of Cu/Pt coreshell particles on carbon cloth (Wei *et al.*, 2008). Also, nickel and copper has comparable lattice parameters values and crystal structure data's. Ni/Pt coreshell was formed by galvanically displacing Ni with Pt particles in displacement solution.

SEM analysis: Figure 8a, shows outer shell materials shows different contrast, i.e., high atomic numbered platinum shows slightly brighter than background diffusive graphene/Ni substrate, which is attributed to be a thin Pt layer deposited on the Ni core to form the core-shell nanostructure. Their presence is confirmed from EDX (Fig. 8c) analysis. The particle size of Ni/Pt coreshell particles is around 40 nm. Figure 8b shows clustered nanoparticles tend to stick together to form a cauliflower like structures on graphene as seen from SEM image.

PdCu/Pt coreshell formation on ERGN: PdCu plating bath compositions (Vinogradov *et al.*, 2001; Rao and Trivedi, 2005) were modified to coat over carbon paper without using any wetting agents. By optimizing the plating bath compositions and different pulse parameters, PdCu alloy can be coated homogeneously with reduced particle size. By using experimental conditions listed in Table 1, one can deposit PdCu nano alloy on carbon substrate.

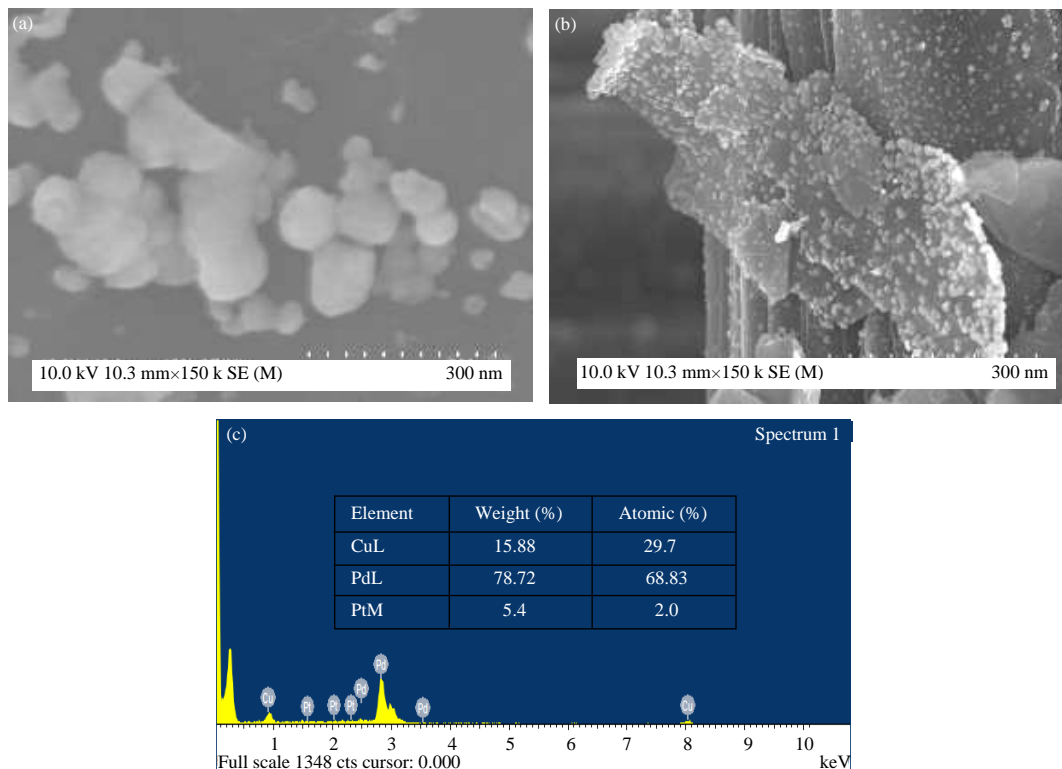


Fig. 9(a-c): (a-b) SEM image of PdCu/Pt coreshell on graphene at different magnifications and (c) EDX of PdCu/Pt coreshell on graphene

SEM analysis: The PdCu coating is characterized using HRSEM and the results are shown in Fig. 9. Core shell Pt particles dispersed on the graphene sheets were clearly seen in Fig. 9a and its particle size is approximately 10-30 nm. Uniform distribution of coreshell nanoparticles on the graphene sheets can be seen in Fig. 9b. EDX (Fig. 9c) confirmed the presence of Pt.

NiW/Pt coreshell formation on ERGN: This plating electrolyte composition (Hu *et al.*, 2009; Lammel *et al.*, 2012) is modified for plating without using any wetting agents. In both compositions, potassium citrate and ammonium chloride were introduced to form complexes with both Ni and W in the electrolyte. In addition, chloride ions are used to reduce the polarization and inhibit passivation of the anode (Lammel *et al.*, 2012). To improve the conductivity, NaCl was added into the electrolyte. The whole plating bath was purged with nitrogen during plating. Ni-W alloys generated by electrodeposition can contain a maximum of 67% W. Low W alloys are usually ascribed to solid solution of W in fcc Ni (Lammel *et al.*, 2012; Krolkowski *et al.*, 2009).

SEM analysis: Figure 10a shows clustered particles which contain platinum shell on NiW core, distributed in the nano scale. The image distinctly displays the background dark image of graphene sheet and bright NiW/Pt coreshell particles. Also shows NiW/Pt coreshell nano particles formed as clusters and embedded in graphene layer. Figure 10b clearly shows the wide-ranging morphology of NiW/Pt coreshell particles forms the structure of cauliflower on graphene sheets. EDX (Fig. 10c) result shows the presence of coreshell particles.

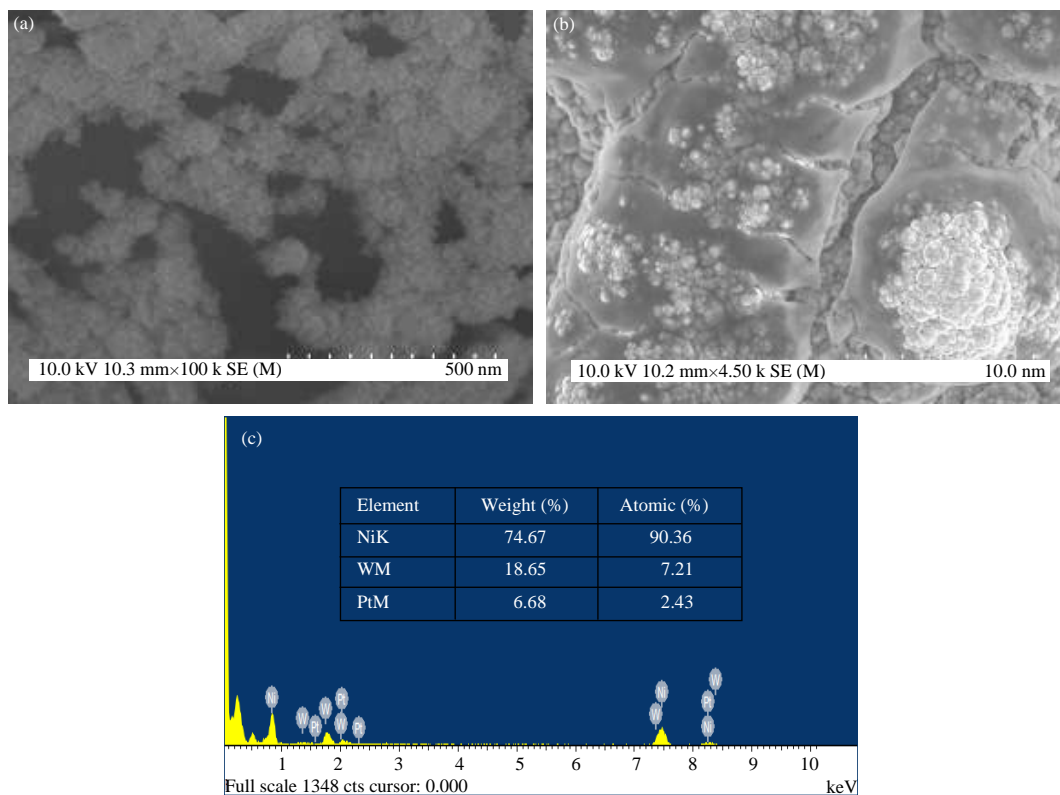


Fig. 10(a-c): (a-b) SEM image of NiW/Pt coreshell on graphene at different magnifications and (c) EDX of NiW/Pt coreshell on graphene

FeNi/Pt coreshell formation in graphene: The displacement of FeNi with Pt is by using non precious metal precursors in an electrolyte solution for core particle deposition and Pt precursor solution for displacement. By this method, one can considerably reduce Pt loading to achieve performance as close as the performance of Proton Exchange Membrane (PEM) based fuel cell with normal Pt loaded electrodes.

SEM analysis: The SEM images of FeNi/Pt catalysts display coreshell nanoparticles at different magnifications as shown in Fig. 11a-b and composition analysis in EDX result (Fig. 11c).

Figure 11a shows a well defined and distinguished coreshell nanoparticles embedded in the thin graphene film with particle size ranges from 10-30 nm. Also found that there is a large contrast variation between graphene surface and coreshell particles. The EDX analysis shows the presence of coreshell particles and indicates complete Pt displacement as Pt weight percentage in the result is 100%. Easily discriminated nano sized coreshell particles on thin graphene films were seen in the image (Fig. 11b).

Macrographs: Macrographs (Fig. 12a-h) of all electrodeposited and Pt displaced samples were taken in high resolution, Single Lens Reflex (SLR) camera. The macrographs reveal the coating area and substrate zones which are easily recognizable at this magnification with the naked eye.

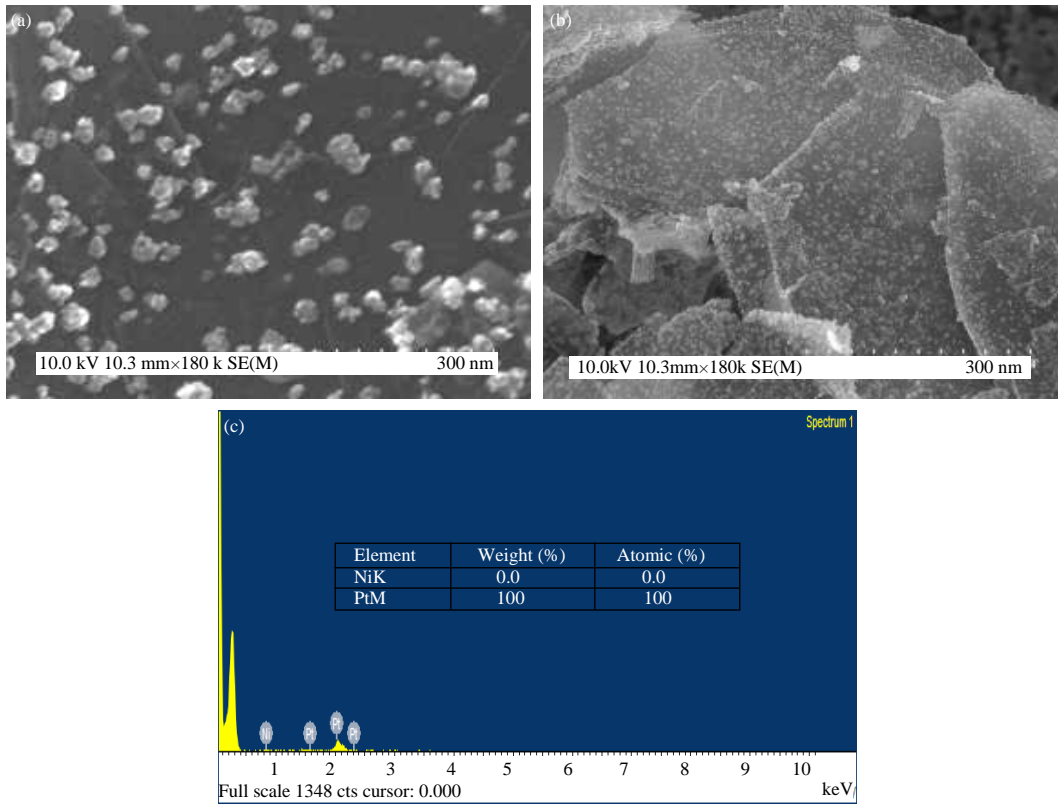


Fig. 11(a-c): (a-b) SEM image of FeNi/Pt coreshell on graphene at different magnifications and (c) EDX of FeNi/Pt coreshell on graphene

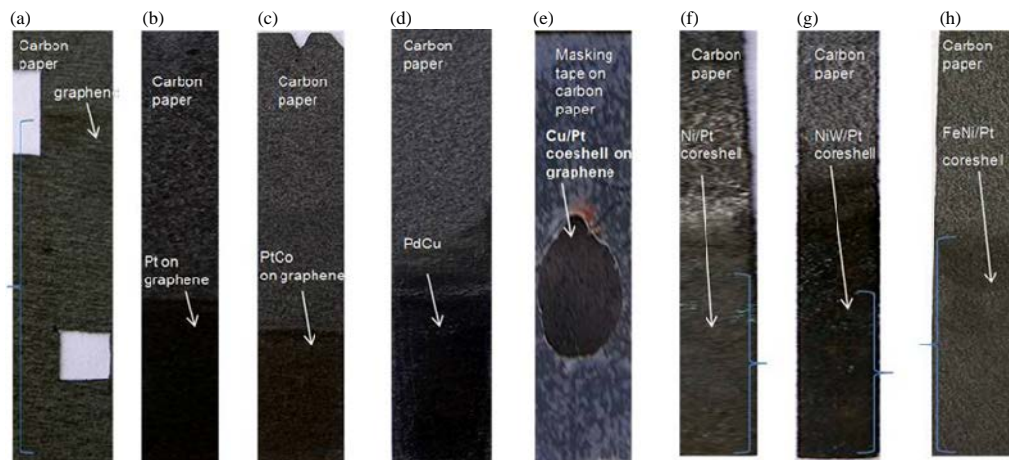


Fig. 12(a-h): Macrographs of coated samples, (a) Graphene coat on carbon paper, (b) Platinum on graphene coated carbon paper, (c) PtCo on graphene coated carbon paper, (d) Cu/Pt coreshell on graphene coated carbon paper, (e) Ni/Pt coreshell on graphene coated carbon paper, (f) PdCu/Pt on graphene coated carbon paper, (g) NiW/Pt coreshell on graphene coated carbon paper and (h) FeNi/Pt coreshell on graphene coated carbon paper

Fuel cell performances: ERGN modified Pt anode and commercial etc make cathode was taken for PEM fuel cell performance using an electro synthesis of graphene supported catalysts is demonstrated in Fig. 1d and e. It is observed that a cell to output a power density of 0.14 W cm^{-2} and current density of 0.64 A cm^{-2} with a low Pt loadings of 0.20 mg cm^{-2} at anode and commercial etc make cathode with loadings 0.3 mg cm^{-2} . Even though the result is comparable with commercial electrodes of anode (Pt loadings 0.3 mg cm^{-2}) and cathode (Pt loadings 0.3 mg cm^{-2}), Pt loading in graphene support is relatively low compared to commercial anode used in another MEA and fabrication cost of membrane electrode assembly with graphene support synthesized by electrochemical route is very much reduced.

That is, it eliminates all difficulties with conventional coating of metal catalyst on the porous electrode, such as selectively depositing metallic catalysts at the sites where catalysts can be fully utilized. The results due to the use of graphene supported Pt catalysts are encouraging which potentially applied to commercial electrode fabrication. This work may further extended to find fuel cell performances of graphene supported pt alloys described in this study.

CONCLUSION

Electroplating capability and the feasibility of Pt-based alloy catalysts on ERGN is noteworthy. A major impediment for commercial viability of PEM fuel cell technologies is due to high costs associated with the precious platinum metal. To encounter this problem, an electrochemical route which is simple, efficient, low cost and fast with green nature is aimed to deposit the desired loading of catalysts through varying pulse parameters and by using catalyst materials in the form of alloys/coreshell structures of high surface area and good conductive graphene support for the design of effective catalysts.

In this study, the electrochemical method was adopted for synthesis of graphene film on the carbon paper and deposition of Pt-based alloys on ERGN. This investigation has unveiled the following observations:

- One step electrochemical synthesis and deposition of graphene on carbon paper using pulse power supply (Two electrode system)
- Pulse electrodeposition of Pt, PtCo on ERGN, using pulse power supply for deposition of nanocatalysts
- Coreshell formation of Pt/Cu, Ni/Pt, PdCu/Pt, NiW/Pt and FeNi/Pt with a galvanic displacement of Pt by electrodeposited alloy over ERGN
- Electroplating of catalyst forms, uniform coating on ERGN which provides effective catalyst utilization
- The nanostructures of elements on surface of graphene were characterized using HRSEM
- These new hybrid composite materials through electroplating have proven to demonstrate excellent potential for commercialization viability over platinum expensive catalysts and conventional materials
- The PEM fuel cell performances of Pt on graphene support, was studied to check the feasibility over commercial electrodes and found that a peak power density of 0.14 W cm^{-2} in the active electrode area of 6.25 cm^2

The surface morphology and composition of the successfully coated graphene and Pt based alloy catalysts were examined using HRSEM and EDX. The surface morphologies of ERGN and graphene supported nanocatalysts were evaluated using SEM images which displays the presence

of nano catalyst and even exist on the surface of thin and transparent graphene sheets. Also, SEM reveals that nano particles deposited only on the surface of graphene exposed to plating solution, not on other areas of graphene and hence, catalyst can be effectively utilized with the ultra low loading of precious catalysts, used in electrodes for applications in fuel cells.

For our graphene based anode the results we await the production of much cheaper and more efficient fuel cells for the future. However, the application of graphene and graphene-based materials in the applications of fuel cells is still in its infancy stage and many challenges ahead. The development of well controlled methods for fabrication of grapheme based electrodes is still in initial level and the first results are only beginning to emerge. It needs more work and a better understanding of the correlation between the electrochemical performance and graphene structures, between the interactions of the grapheme and graphene composite-supported catalysts and their properties, is needed. Our future work will include developing the most suitable methods for synthesizing graphene and graphene composite-based catalysts for effective catalyst utilization for applications to fuel cells. This study accentuates the suitability of this composite coating for future analysis into their application as graphene/carbon composite electrodes in electrochemical energy devices.

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