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Cost effective and energy efficient catalytic support of Co and Ni in Pd matrix toward ethanol oxidation reaction: product analysis and mechanistic interpretation

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Highlights

- Pd₄₀Co₃₈Ni₂₂/C catalyst with closed packed structure bear particle size in the range 2.5 3.5 nm and demonstrate remarkable functional features for ethanol oxidation in DEFC.
- Smart catalytic intervention of the transition metal oxides/ hydroxides in the ternary matrix accelerate the EOR almost toward completion, as evidenced by high yield of acetate and carbonate as oxidation products.
- Power density derived from an in-house DEFC using Pd₄₀Co₃₈Ni₂₂/C is 47.71% higher than with Pd/C and the ternary composition proved to be extremely poison tolerant.

Abstract. The present investigation deals with the comparative analysis of electro-catalytic behaviour of Pt, Pd and ternary combinations of Co and Ni with Pd NPs, supported on vulcan XC72 as the anode component in direct ethanol fuel cell (DEFC) operating in alkaline environment. Catalyst NPs were synthesized by ethylene glycol reduction method and their structure, composition and surface morphology were determined through XRD, EDAX and TEM techniques. The superb catalytic efficiency of PdCoNi/C toward ethanol oxidation reaction (EOR) is ascribed to the catalytic intervention of transition metal ad atoms and their surface oxides, culminating to enhanced electrochemical surface area, preferred OH⁻ adsorption on the surface and remarkable yield of oxidation products (CH₃CO₂⁻ and CO₃²⁻) estimated by ion chromatography. The performance output parameters collectively substantiate not only to the catalytic superiority of the PdCoNi/C catalyst but also affordability to a considerable extent over both the Pt/C and Pd/C catalysts.

Keywords. direct ethanol fuel cell, ethylene glycol reduction, Pd based catalyst, transition metal oxide, ion chromatography.

1. Introduction

Among the fuel cell systems, in recent times, direct ethanol fuel cell (DEFC) has been one of the cleanest choice for energy conversion with high potential advantages that ethanol could offer as a fuel, in respect of 12 electron release during complete oxidation, its abundance from biomass as well as compatibility to the existing fuel infrastructure [1-3]. However, being C2 molecule, electro-catalysis of ethanol is constrained with sluggish oxidation kinetics due to difficulty in C-C bond cleavage and ultimate poor poison tolerance [4]. Efforts are taken to overcome the situation by designing stringent catalysts within multimetallic framework that improve the functional behaviour in terms of electronic as well as, bi-functional effects of the co-metals that proactively take part in the electro-catalysis.

Particularly in search of non Pt catalyst for ethanol oxidation reaction (EOR), Pd has been reported to be an efficient base metal in alkali environment [5, 36]. There are few reports which explain the significant role of oxides and/ hydroxides toward electro-oxidation of alcohols on Pd surfaces. The combinatorial approach towards developing energy efficient electro-catalyst involves incorporation of noble/ non noble metals into the Pd matrix [6- 12].

Fengping Hu et. al. [13] reported on the promoting activity of oxides on modified Pd surfaces with significant performance stability towards ethanol oxidation reactions in alkali medium. Addition of Co to Pd can facilitate the removal of adsorbed ethoxy intermediates due to easy adsorption of hydroxyl groups on Co and/ Co-oxide at lower potentials as reported by S. Han et

al. [14] Bimetallic catalysts are normally found to exhibit higher currents for ethanol oxidation than their single counterparts; however, the oxidation product selectivity is shifted predominantly toward the acetic acid pathway, leading to less efficient use of the fuel [15-17, 25- 26]. Recently, PdAu bimetallic nanoparticles (NPs) with unalloyed nanostructures have been reported by our group, to exhibit much improved electro-catalytic behaviour in EOR study [18]. Shen et. al. [19] reported ternary PdIrNi nano catalyst with increased peak power density compared to the monometallic Pd nano catalyst. Bambagioni et. al. synthesized Pd based ternary alloys in alkaline medium and demonstrated promising EOR activities on Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C catalysts [20, 27]. In several of our earlier reports we have discussed on the involvement of Ni and its oxide/hydroxide species as well as Au NPs in the EOR sequence over PdNi and PdNiAu NPs [21, 22]. Besides all these, the introduction of a second or third metal or metal oxide promoter, particularly from the transition metal series, to a non Pt base matrix has been rarely reported.

In course of searching cheap and efficient electro-catalyst for ethanol oxidation in fuel cell, in this attempt, we have synthesized carbon supported nano-structured ternary PdCoNi catalyst for the study of EOR and demonstrated the concerted effort of Co and Ni toward promoting the catalytic performances of the ternary matrix. The single and ternary catalyst matrices were developed through the reduction of the respective metal chlorides (Pt, Pd, Co and Ni) by modified ethylene glycol reduction method [23-24, 28, 37]. Physical and electrochemical characterizations were performed in order to determine particle size, morphology, identify phases and derive electrode kinetic behaviour of the synthesized materials toward EOR in alkaline electrolyte at room temperature. The working electrolytes were further subjected to ion chromatographic analysis to identify and estimate the products formed during the course of EOR,

thereby elucidating the mechanistic pathway. Finally, the single cell testing is carried out using the membrane electrode assembly (MEA) comprising of synthesized catalysts as anode, Pt/C catalyst as cathode and the alkaline anion exchange membrane sandwiched in between.

2. Experimental Section

2.1. Synthesis of Catalysts

A 40:60 catalyst-support ratio was maintained during synthesizing the catalyst regime by taking appropriate amount of Vulcan XC-72 carbon (Carbon India Ltd., Brunauer-Emmett- Teller (BET) surface area, 288 m² g⁻¹) and the metal precursors H₂PtCl₆, 6H₂O, PdCl₂,xH₂O, NiCl₂(Arora Matthey Ltd.) and CoCl₂,6H₂O (A.R, E Merck, Germany) in their respective proportions. The mixture was subjected to chemical reduction using ethylene glycol (E-Merck) solution at 160^oC temperature and in alkaline pH to obtain the respective metallic deposits of Pt, Pd, Ni, Co as well as PdCoNi (1:1:1). Similar synthetic procedure was followed for developing PdCo/C and PdNi/C binary catalysts used only for surveying the electrochemical surface of the catalysts and to figure out the additional contribution of the transitional metals in the ternary matrix.

2.2. Surface Morphology and Structural Characterization

The crystalline structures of the supported catalysts were revealed through the powder X-ray diffraction (XRD) technique using a Rigaku (mini flex II) parallel beam X-ray diffractometer operating with Cu K α radiation ($\lambda = 0.1540$ nm) generated at 35 kV and 30mA. Scans were recorded at 1° min⁻¹ for 2 θ values between 20° and 90°. The XRD patterns were analyzed following the JCPDS file, and Scherrer and Bragg's formulae were used to calculate the mean diameter and the lattice parameter of each of the catalyst. The chemical compositions of the

multimetallic catalyst layers were determined by energy-dispersive X-ray spectroscopy (EDX) using a Link ISIS EDX detector (Oxford Instruments, UK) coupled with the transmission electron microscope. The catalysts suspended on a standard carbon-coated Cu grid were subjected to high-resolution transmission electron microscopy (HRTEM) using JEOL JEM 2100 operating at an accelerating voltage of 200 kV. Specimens for TEM analysis were prepared by suspending the particles in alcohol in an ultrasonic cleaner (Model AU-30C, 4 L capacity, 100 W, 28 KHz, 130 VA, timer 15 mins, Eyela, Tokyo, Rikakikai Co., LTD). A drop of the suspension was deposited onto a standard carbon-coated Cu grid (GCU300, 300 mesh square, ProSciTech, Australia) and allowed to dry before being inserted into the microscope. The particle size distribution (histograms) was obtained by the observation of about 300 particles from the four different locations of the corresponding TEM images.

2.3. Electrochemical Studies

The fabrication of the electrodes included usual method of preparing catalyst ink by mixing 2propanol (GR, Merck) with an appropriate amount of the catalyst in 5 wt% Nafion ionomer (Eloctrochem. Inc., USA) followed by sonication. A calculated amount of this slurry was micropipette out onto the graphite plate (GLM grade, Graphite India Ltd.) of 0.65 cm² surface area maintaining a constant catalyst loading of 0.77 mg cm⁻². Electrochemical measurements were recorded by the help of a microprocessor controlled potentiostat/ galvanostat (PG stat 12 and FRA modules, Ecochemie BV, Netherlands) in a three electrode assembly cell containing 1 M ethanol (Merck, A.R) in 0.5 M NaOH solution and consisting the synthesized catalysts as the working electrodes, bright Pt-foil (10 mm × 10 mm) counter electrode and mercury/ mercurous oxide (Hg/HgO) reference electrode with respect to which the potentials in this article are expressed.

2.4. Estimation of Reaction Products

The ion chromatography system (Metrohm's Advanced Modular Ion Chromatography) consisting of a L-7100 pump (Metrohm Ltd.), a conductivity detector, and Metrosep A Supp 5-250 and Metrosep A Supp 4-550 organic acid columns was employed to quantify the yields of acetate and carbonate ions produced during the electrolysis by taking aliquots from the working electrolyte after polarization at a constant potential of -300 mV for 1 hr at room temperature. The entire work of electrochemical characterization and the chromatographic estimation were carried out in inert atmosphere by purging N_2 (XL grade from BOC India Ltd.) into the solution before experimentation and also maintaining N_2 atmosphere within the working cell set up.

2.5. Performance Testing of DEFC

Membrane Electrode Assembly (MEAs) was prepared by hot pressing and arranged with synthesized catalysts (as anode), alkaline anion exchange membrane, AEM (A-006, purchased from Tokuyama Corp. Japan) and Pt/C (40% metal/C as cathode) catalyst. Metal loading is same (1.0 mg cm⁻² Pt loading) for both the anode and cathode catalysts and the exposed area of the MEA is 1cm². Fuel cell testing was performed at 40 °C with the test station of Fuel Cell Technologies Inc, USA. Flow of alkaline ethanol solution to the anode is maintained at 1.0 mL min⁻¹, while oxygen is fed into the cathode chamber at a flow rate of 100 cm³ (STP) min⁻¹.

3. Results & Discussion

3.1. Electron Microscopy and X-ray Diffraction Studies

Figure 1 shows the typical EDX spectrum of the as-prepared PdCoNi/C catalyst. The compositional analysis is given in **Table 1**. The EDX analysis of the metallic phase demonstrates the presence of each of the individual metals with proportionate existence of 40:38:22 in the PdCoNi/C matrix. The EDX composition of the as-prepared PdCoNi/C catalyst more or less agreed with the precursor bath compositions except that Ni was less deposited compared to the other two metals.

Figure 2a shows the XRD patterns of Pd/C, Co/C, Ni/C and ternary catalyst Pd40C038Ni22/C. Each of the XRD patterns show characteristic peaks of face centered cubic (fcc) crystalline facets of Pd, Co and Ni which exhibit diffraction of (111), (200), (220), (311), and (222) facets corresponding to fcc crystal structure according to the respective JCPDS file 46-1043 for Pd, 15-0806 for Co and 04-0850 for Ni. The diffraction peaks of Pd/C like Pd (111), Pd (200), Pd (220), and Pd (311) appear at 39.85°, 46.4°, 67.924° and 81.8° respectively, for Co/C the respective facets are (111), (200) and (220) corresponding to $2\theta = 45^{\circ}$, 52.02°, and 75.77° and for Ni/C the (111), (200) and (220) facets appear at $2\theta = 43.79^{\circ}$, 51.02° and 74.74° respectively. The largest peak shift is noticed for Pd40C038Ni22/Ccatalyst for which Pd peaks (111), (200), (220), and (311) are shifted 0.2° right, indicating possible alloy formation in the ternary matrix. For Pd₄₀Co₃₈Ni₂₂/Cthe shifted peak with respect to Pd/C corresponded to 2θ values at 40.05⁰ for (111) (Figure 2b), 46.67° for (200), 68.3° for (220), 81.83° for (311) and 86.51° for (222) facets. Similarly the peak shifting inPd40C038Ni22/Cwith respect to Co/C are obtained at $2\theta =$ 45.10°(111), 52.42°(200), 76.0° (220) and with respect to Ni/C, obtained at $2\theta = 44.20^{\circ}(111)$, 51.26⁰(200) and 78.01⁰ (220).

Some of the critical oxide phases identified (**Figure 2c**) in the XRD pattern of the ternary matrix are Ni₂O₃H (141, JCPDS file 40-1179), NiOOH (108, JCPDS file 06-0075), NiOOH (211 and

121 JCPDS file 27-0956), Co₃O₄(511), Ni(OH)₂ (110), NiOOH (310), Co₃O₄ (440) and Ni(OH)₂ (220, JCPDS file 22-0444) corresponding to the peaks appearing at 44.36⁰, 51.58⁰, 54.61⁰, 59.71⁰, 60.87⁰, 62.14⁰,65.0⁰ and 70.78⁰ respectively. The addition of Ni and/or Co into the Pd, eventually suppresses the growth of the ensemble of metallites and the particle size is found to decrease in the multimetallic matrix, as calculated using Scherrer's equation D=0.9 λ / B cos θ considering the Pd (111) peak, where D is the crystallite size nm, λ is the wave length (0.154 nm for Cu-K α), B is the full width at half-maximum (FWHM) (in radians) and θ is the diffraction angle. Depending on the XRD results, the interplanar distance *dhkl* with Miller Indices (*hkl*) for the catalysts were estimated according to Bragg's equation n λ =2dsin θ . It is discernible from **Table 1** that incorporation of transition metals into the Pd result in decreasing lattice parameter, inter planer distance and average crystallite size indicating alloy formation and /or close pack multimetallic matrix formulation.

Figure. 3a and **3b** shows the TEM images and histogram (size distribution) as derived from ensemble of 300 particles of the Pd/C and Pd₄₀Co₃₈Ni₂₂/Ccatalysts. As observed, the metal particles on both the catalysts exhibit spherical shape and are well dispersed on the meso porous carbon powder. The size distribution range from 1 to 7 nm and the average particles size in the catalyst matrix Pd₄₀Co₃₈Ni₂₂/C is 3.6 nm which corroborates with the XRD data. The SADP represented by the inset of **Figure 3b** indicates the formation of nano-phases of Pd₄₀Co₃₈Ni₂₂/C with good crystallinity and the rings are indexed for an fcc crystal structure. **Figure 3c** shows the typical fringe pattern of the Pd/C nano-particles indicating (111) plane of Pd. Some well defined fringe-finger prints (**Figure 3d**) of Pd₄₀Co₃₈Ni₂₂/C were used to measure the inter-planar d-spacing with the help of corresponding FFT pattern (**Figure 3d inset**) where from the lattice spacing are found to be around 0.227, 0.233 and 0.204 nm, corresponding to (111) planes of Pd,

Co and Ni respectively. Although XRD results indicate alloy formation, distinct existence of trimetallic phases of Co, Ni & Pd are also evidenced from the fringe patterns. This signifies that the catalyst is not entirely composed of perfectly alloyed particles throughout the matrix but there is possibility of the simultaneous existence of unalloyed composite particles of Pd, Co, Ni along with the alloyed phases. A distinct quenching of the particle size in the trimetallic composite is worth noting, 58 % from XRD and 41% from TEM analysis, compared to the single metal catalyst. This is attributed to the comparatively lower atomic radii of the transitional cometals, Co (1.25 Å) and Ni (1.25 Å) compared to Pd (1.37 Å).

3.2. Voltammetric studies

Figure.4 shows the cyclic voltammograms (CV) for Pt/C, Pd/C, Co/C, Ni/C and Pd₄₀Co₃₈Ni₂₂/C catalysts obtained in 0.5 M NaOH solution at a scan rate of 50 mVs⁻¹ within the potential window -1000 mV to 800 mV. The hydrogen region is prominent for Pt/C, Pd/C and the ternary systems while no significant contribution is made by the bare Co and Ni in this region. The respective CV of Co/C and Ni/C however demonstrate the oxide formation and oxide reduction region as their special features.

The voltammogram of Pd40C038Ni22/C catalyst exhibit enormous current density in the anodic and cathodic sweeps compared to the single counterparts. In the anodic sweep considerable expansion is observed for the critical regions like hydrogen adsorption region (HAD) followed by premature double layer charging and pronounced current output in the oxide formation region, unusually aggravated with the simultaneous effect of transition metals Co, Ni and Pd itself. The double layer region covers a considerable potential range (480 mV) from -270 mV to 210 mV. The colossal oxidation current beyond 0.270 V is one of the remarkable features of the surface functional behavior of the ternary catalyst. The oxide formation within potential span

350-600 mV resembles the pattern of Co/C as well as Ni/C catalysts, however with much amplified current production indicating the formation of an oxide reservoir in the multimetallic catalyst matrix. This is distinctly reflected in the reverse scan where the usual Pd-oxide reduction appears with enhanced current output in the potential range -200 mV to -650 mV and an additional cathodic peak appears with much broader area and high current output indicating reduction of co-metal oxides (Co and Ni) in the potential range 410 mV to -150 mV, henceforth designated as Transition Metal Oxide Reduction (TMOR) _{Co,Ni} region. The expanded area in the cathodic reduction regions, collectively for TMOR as well as Pd oxide reduction become an added advantage in course of promoting EOR kinetics as discussed later.

The electrochemical surface area (ECSA) of the catalysts were derived from the voltammgrams by integrating the charge on hydrogen adsorption–desorption (HAD) and adsorbed oxide reduction (AOR) regions and summarized in **Table 2** [21, 29]. Although Pt surface exhibits considerable ECSA values, it ultimately suffers from poor poison tolerance, whereas ECSA values for both HAD and AOR regions were extraordinarily increased for Pd40C038Ni22/C. This may be a reflection of particle size diminution in the mixed metallic matrix as discussed earlier. Moreover, the special feature of the huge oxide store discernible in the forward scan may also be responsible for the enhanced cathodic current in the AOR region in the reverse sweep.

For better understanding of the synergic effect manifested in the voltammetric feature of the ternary matrix, a magnified view of the voltammogram of the single metal and ternary catalyst (Pd40C038Ni22/C) are presented in **Figure S1** (supplementary material) along with the probable surface reactions. It may be understood that the charges corresponding to the different regions of the voltammogram reflects the relative electro-chemical activity of the catalyst surface. The values obtained from the CV plots are summarized in **Table 3**. The most interesting phenomena

for the ternary catalyst is that it produces enormously large area in the $(TMOR)_{Co,Ni}$ region that add testament to the superior surface electro-activity of this ternary composition.

At this stage, for precise screening of the electrochemical surface activity and to elucidate the multi coupled effect of Co & Ni in the Pd matrix, voltammograms were also recorded with binary PdCo/Cand PdNi/C catalysts in 0.5 M NaOH solution under similar conditions and demonstrated in **Figure S2** (supplementary material). The binary catalysts also show similar characteristic feature in the TMOR region, however not as much enlarged as in the case of the combined ternary matrix. It is seen from **Table 3** that the charges exhibited by the ternary catalyst, especially in TMOR region, is almost 4.6, 4.1, 8 and 6.5 times greater than those obtained with the respective catalysts Co/C, Ni/C, PdCo/C and PdNi/C under similar potentiodynamic condition. Hence, the individual contributions of Co and Ni toward formulating a catalytically efficient ternary (PdCoNi) matrix, is an advantageous conjunction translating to fabulous increase in the area [(TMOR)_{Co,Ni}+ AOR_{Pd}] which in effect becomes extremely useful in promoting EOR kinetics as recorded by the outstanding electro-efficiency of this particular combination.

In fact the concerted effort of each of the co-metals in this multimetallic ensemble creates structurally and electronically favored ternary matrix (Pd40Co38Ni22/C) with ample electrochemically active reaction centers. The smaller particle size and uniform size distribution throughout the catalyst matrix obtained from XRD and TEM analysis are also in tandem with the higher ECSA values for the Pd40Co38Ni22/C catalyst.

Infact the electronic effect in the combined matrix also plays an important role in propagating the EOR as discussed in the next section. The charge distribution among the co-metals is depicted in **Scheme1**. Due to higher ionization energy of Pd (8.34 eV) than Co (7.88 eV) and Ni (7.63 eV),

12

the electronic charge transfer may take place from Ni to Pd, Co to Pd and Ni to Co to Pd. This induces extra positive charge on Ni and Co atoms and facilitates the formation of different oxides/hydroxides of Co and Ni while δ^- charges on Pd sites facilitate easy anchoring of the ethanol molecule undergoing the electro-oxidation.

The existence of NiOOH species on Ni containing noble metal catalyst surface is well known, and this moiety actively takes part in hydrogen spillover and increases the charge in that region. On the other hand, Co, having affinity toward forming multivalent oxides, provides substantial oxide coverage throughout the catalyst matrix.

Figure 5 represents the characteristic voltammograms of EOR in the potential range -1 V to 0.8 V on Pt/C, Pd/C, Co/C, Ni/C and Pd40C038Ni22/C. The voltamograms clearly demonstrates that the combined formulation of the cheap transition metals and Pd can greatly enhance the electrochemical activity for ethanol oxidation in alkaline medium. Form the inset of Figure 5, the onset potential (Eonset) of EOR follow the order Pd40Co38Ni22/C< Pt/C <Pd/C. As expected, the renewed oxidation (in the reverse sweep)on the ternary catalyst starts much earlier (less – ve potential) compared to the single metal catalyst and the current density (I_{renewed}) and the onset potential (Erenewed onset) for the renewed oxidation follow the positive potential shift PdCoNi/C>>Pd/C> Pt/C as shown in Figure 6a and 6b. The respective forward and renewed oxidation peak current densities are 108 mA cm⁻² and 83 mA cm⁻² for Pd₄₀Co₃₈Ni₂₂/C, 75.9 mA cm⁻² and 32 mA cm⁻² for Pt/C while 65mA cm⁻² and 28 mA cm⁻² for Pd/C. Figure 7 shows that the forward and renewed oxidation peak potential difference is much reduced in case of $Pd_{40}Co_{38}Ni_{22}/C$ which is a typical behavior that translates to catalytic superiority of the ternary composite over the others. All these electrochemical features like higher peak current and reduced value of E_f-E_b, the early onset of the renewed oxidation reflect the excellence of the

composite in promoting the EOR kinetics by oxidative removal of the carbonaceous residues on the multimetallic matrix, designed with non Pt noble and non noble transition metals.

3.3. Chronoamperometic studies and estimation of oxidation products

The intermediates produced during the oxidation of ethanol get adsorbed on electro-catalysts and poison their catalytic activity and in effect destroy their stability. Hence to investigate upon the deactivation of the catalytic surface, chronoamperometric studies were carried out with Pd/C and PdCoNi/C catalysts in the working electrolyte at a fixed potential of -0.3 V for 3600 s (**Figure 8a**).

The resulting curves indicate that the PdCoNi/C electrode produce much higher EOR current density after 3600 s while the poisoning rate (δ) is reduced to half (0.00479 % per second) the value obtained for Pd/C(0.01 % per second). The derivative Anson's plot (*Q Vs t*^{1/2}, **Figure 8b**) allows the determination of the amount of charge involved in the process for single and ternary catalysts whereby faster electrolysis is demonstrated in case of the multimetallic matrix.

Figure 9a & 9b shows the ion chromatograms for the product analysis during EOR carried out on Pd/C and Pd₄₀Co₃₈Ni₂₂/C electrodes for a period of 1 h at room temperature. The respective products, acetate and carbonate formed during the oxidation of ethanol were estimated and summarized in **Table 4**.

On the basis of the remarkably high yield of acetate and carbonate (6.1 and 6.7 times than on Pd/C and 4.8 and 5.7 times than on Pt/C) on the ternary catalyst, we have tried to outline a mechanistic pathway for the oxidation of ethanol, assisted by the conjugate effort of the cometals in the trimetalic ensemble of NPs (Pd, Co and Ni) each contributing to the kinetic input

for the electron extraction process, where 60% of the catalyst loading is comprised of transition metals.

3.4. Mechanistic overview of EOR

Pd NPs have intrinsic ability to absorb OH⁻ at lower potentials in alkaline electrolyte while Co and Ni both are oxophilic and enrich the catalyst surface with oxy / hydroxy species [Co₃O₄, CoO, NiOOH, Ni₂O₃H, Ni(OH)₂ etc] that play vital role in activating the surface for favourable electrochemical oxidation of ethanol molecule.

The fair possibilities of EOR to proceed along parallel mechanistic pathways are: (i) Faster removal of intermediate species $(CH_3CO)_{ads}/(CH_3O)_{ads}$ on the OH studded electrode surface at low potentials leading to significant amount of acetate production as well as CO_3^- formation to some extent (ii) catalytic intervention of Ni through Ni(OH)₂ species and (iii) assistance of Co oxide rich network by forming methoxy linkage that enable to reach the ultimate CO_2 production. The possible reaction sequences are highlighted.

(i) Water activation at low potential assisting EOR (rigorous involvement of OH ads)

$$(CH_3CH_2OH)_{sol} \to (CH_3CH_2OH)_{ads} \tag{3}$$

$$OH^- \to (OH)_{ads} + e^- \tag{4}$$

$$(CH_3CH_2OH)_{ads} + 3OH^- \rightarrow (CH_3CO)_{ads} + 3e^-$$
(5)

$$(CH_3CO)_{ads} + (OH)_{ads} \to CH_3COOH \tag{6}$$

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \tag{7}$$

$$(CH_3C00^-)_{ads} + 20H^- \rightarrow (CH_30)_{ads} + CO_2 + H_20 + 3e^-$$
 (8)

$$(CH_3COOH)_{ads} + 30H^- \rightarrow (CH_3O)_{ads} + CO_2 + 3H_2O + 3e^-$$
 (9)

The adsorbed carbonaceous species (CH₃O)_{ads} readily interact with further OH-leading to surface poisoning by (CO)_{ads}.

$$(CH_3O)_{ads} + 3OH^- \to (CO)_{ads} + 3H_2O + 3e^-$$
 (10)

However at suitable pH condition and with adequate supply of OH^- , $(CO)_{ads}$ is likely to get oxidized, producing the ultimate species CO_3^{2-} .

$$(CO)_{ads} + (OH)_{ads} + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + e^-$$
 (11)

(ii) Role of Ni and its oxides

The contribution of Ni oxy/ hydroxyl species towards assisting EOR has been reported in our earlier work with PdNiAu [8, 21, 30]. There are few reports that indicate Ni(OH)₂ and NiOOH bear high electron and proton conductivity. In alkaline medium, Ni(OH)₂ can produce NiOOH species by releasing H⁺ which combines with OH⁻ to produce water while absorption of H⁺ by NiOOH may also take place to produce Ni(OH)₂. Thus a rapid equilibrium between the Ni(OH)₂/NiOOH species is attained through the spillover of hydrogen, which eventually gears up the oxidation of ethanol on the multimetallic matrix [31-32].

The catalytic intervention of NiOOH [33-34] toward ethanol oxidation is demonstrated in the following reaction sequences and also schematically represented (**Scheme 2**):

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
(12)

$$NiOOH + CH_3CH_2OH \rightarrow CH_3CH_2O + Ni(OH)_2 + e^-$$
(13)

$$NiOOH + CH_3CH_2O \rightarrow CH_3CHO + Ni(OH)_2 + e^-$$
(14)

$$NiOOH + CH_3CHO \rightarrow CH_3CO + Ni(OH)_2 + e^-$$
(15)

$$NiOOH + CH_3CO \rightarrow CH_3COOH + Ni(OH)_2 + e^-$$
 (16)

Furthermore, Ni(OH)₂ is known to generate NiO that exists in the dimeric form (NiO)₂ $[Ni(OH)_2 \rightarrow NiO + H_2O \& 2NiO \rightarrow (NiO)_2]$, assisting the ethanol oxidation process as has been elaborately discussed in our earlier study on EOR over PdNi/C catalyst [22].

It was suggested that $(NiO)_2$ moiety drags the reaction to the ultimate CO_3^{2-} formation in alkaline medium by direct or indirect pathway (i) conversion of ethanol to acetaldehyde (ii) conversion of acetaldehyede to acetic acid and (iii) conversion of acetaldehyede to carbonate.

(iii) Role of Co and its oxides

In case of Co/Co oxide existing in the matrix there is possible formation of [–O–Co–O–Co–O–] type network which effectively can take part in the ethanol oxidation process [35]. In one of our previous articles with PtPd/MoO₃-Polypyrrole matrix, such kind of linkage in MoO₃ has been reported to be instrumental in the electro-catalytic oxidation of ethanol.

In the present case, we suggest that the intermediate $(-CH_3CO)_{ads}$ species gets associated with the metal oxide network to produce the methoxy linkage (equation17). The latter interacts with $(OH)_{ads}$ on the metal matrix (M-OH) whereby electron extraction is facilitated and reaction proceeds toward the final release of CO₂ (equation 18-19) as described in the following reaction sequences and also represented schematically. (Scheme 3)

$$M(CH_3CO) + O - Co - O - Co \to CH_3O - Co - O - Co + M - CO$$
(17)

$$CH_3O - Co - O - Co + M - OH \rightarrow CH_3O - Co - O - Co - OH + M$$
 (18)

$$CH_3O - Co - O - Co - OH \xrightarrow{-4e} CO_2 + Co - O - Co + 4H^+$$
(19)

The **Scheme 4** represents an overall model for EOR phenomena on the multi-metallic catalyst matrix. The addition of transition metals to Pd NPs remarkably improves the kinetic efficacy of EOR by virtue of their excellent co-catalytic activity in terms of rapid elimination of carbonaceous residues from the surface and propagating the reaction toward completion.

For the further evidences in support of the electro-catalytic activities, typical Nyquist plots are derived from impedance spectra of Pd/C and Pd40Co38Ni22/C at the anodic potential of -300 mV. Detailed discussions related to impedance study have been included in the supplementary material.

3.5. Electrical performance of DE(AEM)FC

Finally the performances of the catalysts (**Figure 10**) are tested in the single cell of the fuel cell test station. Open circuit voltage (OCV) and maximum current density for Pd/C catalyst are found to be 0.76 V and 213mAcm⁻² while for the ternary catalyst the values are 0.83 V and 263 mA cm⁻² respectively. Even when the Pd loading is 60 % reduced to in the ternary catalyst, the performance characteristics (OCV and current density) are far beyond those for the individual metal catalyst. Obviously the intervention of Co, Ni towards electro-catalysis is further reflected in the significant power density ~39.44 mW cm⁻²) obtained for the ternary catalyst compared to 26.70 mW cm⁻² for bare Pd catalyst.

4. Conclusion

In this investigation, carbon supported ternary PdCoNi nano-catalysts were synthesized by the simultaneous ethylene glycol reduction method and the determination of morphology, structure and composition of the NPs reveal that the trimetallic particles composed of alloyed and unalloyed phases bear average size in the range 2.5-3.5 nm and indicate ample existence of transition metal oxides as vital component of the catalyst materials. A set of electrochemical techniques like cyclic voltammetry, potentio-dynamic polarization, chronoamperometry and the performance screening in an in house fabricated DE(AEM)FC demonstrates the outstanding functional behaviour of the mixed metallic matrix particularly with the incorporation of Ni and Co to Pd and the latter being reduced to 40% in the catalyst matrix. The transition metal/ metal oxides take proactive role in the electro-catalysis and provide multifunctional activities in tandem with Pd in the matrix. The ethylene glycol reduction proved to be an efficient route for fabricating the catalyst NPs. A series of multiple reactions occur in coordination with the reaction centers created at the self-designed multimetallic matrix which enable EOR to progress toward completion. Overall, the synergy of the bifunctional effect and the electronic charge distribution enable the Pd40Co38Ni22/C catalyst composition to promote ethanol oxidation at a lower energy and faster rate than the single and binary catalyst counterparts.

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Figure.1. Typical EDX spectrum of Pd40C038Ni22/C catalysts.



Figure.2. (*a*) X-ray diffraction patterns of Pd/C, Co/C, Ni/C & Pd₄₀Co₃₈Ni₂₂/C catalysts. Magnified view of the diffraction peaks at 2θ (*b*) 35° to 45° and (*c*) 44° to 74° .



Figure. 3 TEM image with histogram (a) Pd/C (b) Pd₄₀Co₃₈Ni₂₂/C, Inset: SADP, (c) Fringe pattern of Pd/C, (d) Fringe pattern of a single particle having three different d-spacing for Pd₄₀Co₃₈Ni₂₂/C, inset: FFT pattern of the corresponding fringe pattern.



Figure.4. Cyclic voltammograms of Pt/C, Pd/C, Co/C, Ni/C and Pd₄₀Co₃₈Ni₂₂/C in 0.5 M NaOH recorded at scan rate 0.05 Vs⁻¹.



Figure.5. Cyclic voltammograms of EOR on single and ternary catalysts. Sweep rate: 50mVs^{-1} . Inset: Bar diagram of the onset potential recorded at current outputs 4.00 mA cm⁻² for Pt/C, Pd/C and Pd₄₀Co₃₈Ni₂₂/C catalysts.



Figure.6. (a) Renewed peak current density ($I_{renewed}$) and (*b*) onset potential for renewed ethanol oxidation on Pt/C, Pd/C and Pd₄₀Co₃₈Ni₂₂/C catalysts.



Figure.7. Anodic and cathodic peak potential difference from the voltammograms of EOR on Pt/C, Pd/C and Pd₄₀Co₃₈Ni₂₂/C catalysts.



Scheme1. Schematic representation of the charge distribution on closed packed model structure of Pd₄₀Co₃₈Ni₂₂/C catalysts.



Figure.8. (a) Chronoamperograms recorded for 1 h and (b) charge density vs $t^{1/2}$ plots for Pd/C and Pd₄₀Co₃₈Ni₂₂/C.



Figure.9. Typical ion chromatograms for estimation of (a) acetate and (b) carbonate produced during electro-oxidation of ethanol on Pd/C and $Pd_{40}Co_{38}Ni_{22}/C$ electrodes.



Scheme3. Intervention of Co oxide towards EOR.



Scheme 4. Model representation of overall ethanol oxidation pathways on Pd40C038Ni22/C catalyst.



Figure.10. Polarization and power density plots for DE(AEM)FC with Pd/C and Pd₄₀Co₃₈Ni₂₂/C anode catalysts.

Electro- catalysts	Pd:Co:Ni (nominal weight ratio)	Composition From EDX	Interplanar Distance	Lattice parameter /Å	Average crystallite size / nm	
		(atomic %)*	(Å)		XRD	TEM
Pt/C	1:0:0	-	2.266	3.925	3.04	
Pd/C	1:0:0	-	2.259	3.913	5.57	6.1
PdCoNi/C	1:1:1	Pd: 40; Co: 38; Ni:22	2.246	3.892	2.32	3.6

Table1. Physical properties as derived from XRD, TEM, EDAX of the Pt/C, Pd/C, Pd₄₀Co₃₈Ni₂₂/C electro-catalysts.

Flectro-catalysts	ECSA (m ² g ⁻¹)			
Electro-catalysts	HAD	AOR		
Pt/C	33.4	43		
Pd/C	19.2	44.6		
Ni/C	-	-		
Co/C	-	-		
Pd40C038Ni22/C	56.1	60.2*		

*Obtained from the contribution of Pd oxide reduction excluding TMOR.

Table2. ECSA (HAD, AOR) for the respective catalysts Pt/C, Pd/C, Ni/C, Co/C and Pd₄₀Co₃₈Ni₂₂/C.

Oxidation- reduction regions	Charge (µCcm ⁻²) x 10 ⁻¹ of the catalysts obtained from cyclic voltammogram						
voltammogram	Pt/C	Pd/C	Co/C	Ni/C	PdCo/C	PdNi/C	Pd40C038Ni22/ C
Oxide formation	1059.01	470.98	578.02	426.66	-	556.62	2823.82
Transitional metal oxide reduction (TMOR)	-	-	469.12	529.56	277.54	337.24	2188.44

Table3. Charges under the critical areas covered by the respective catalysts Pt/C, Pd/C, Ni/C,

Co/C and Pd₄₀Co₃₈Ni₂₂/C in the CV plot.

Catalyst	CH ₃ COO ⁻ (ppm)	CO ₃ ⁻² (ppm)
Pt/C	51	107
Pd/C	40	91
Pd40C038Ni22/C	245	610

Table4. Estimated yield of acetates and carbonates on Pt/C, Pd/C and Pd40C038Ni22/C catalysts.