Chapter 5

PdM/C (M=Cu, Ni, Co) NANOPARTICLES FOR ELECTROCHEMICAL OXYGEN REDUCTION AND OXYGEN EVOLUTION REACTIONS
Outline
Increasing energy demands lead to the stimulation in the research related to the production of alternative and clean fuels with zero emissions [1-4]. In the last few decades, the growing demand of low cost renewable energy has raised significantly in terms of alternative energy conversion as well as storage devices as clean and sustainable energy sources. A considerable amount of research is being conducted on fuel cells as a clean, alternative energy source [5-7]. Proton exchange membrane fuel cells (PEMFCs) are receiving more attention due to their high energy density, convenient operations and environmental friendly characteristics [8-10]. However the use of expensive and rarely available Pt electrocatalyst in PEMFCs motivated researchers toward design and development of non-platinum electrocatalysts [11]. Eventually, the search for new materials for the oxygen reduction reactions (ORR), a sluggish reaction that occurs in the cathode which requires high content of Pt is a major concern [12, 13]. Electrochemical reduction of oxygen is crucial and a key challenge for various sustainable energy technologies, such as, fuel cells and metal-air batteries [14-17].

Scheme 5.1 Representation of ORR as well as OER over synthesized NPs.
Although Pt and Pt-based nanomaterials are proven to be promising candidates for ORR with high efficiency and work function, the outline of the problem arises from its slow kinetics and other problems like the cross-over and poisoning effect [18, 19].
Hence, development of non Pt-based electrocatalyst needed significant attention. Palladium and palladium based metal nanoparticles (NPs) have attracted great interest in scientific research and industrial applications, owing to their unique large surface-to-volume ratio and quantum-size effects [20-22]. To substitute the expensive Pt-based ORR electrocatalyst, recent advances have been made to develop Pd-based bimetallic nanoparticles for their high catalytic activity and stability for ORR resulting from their catalytic synergistic effect [23, 24]. Alloying of low-cost earth-abundant transition metals, such as, Cu [25], Co [26], Ni [27] with highly active Pd has significantly influenced in the close proximity of bimetallic alloy nanostructures for the application of different energy related reactions. It is clearly evident that mixing of two or more metals together enhances catalytic performance as they have distinct properties from their monometallic counterparts [28, 29]. Compared to the other transition metals Cu nanocatalysts have been reported in a number of industrial and chemical applications, for example, catalytic reforming, different fuel cell reactions, catalytic reduction reactions etc. [30-32]. In the current study, we develop Pd$_x$M$_y$ (M=Cu, Ni, Co) and (x, y =1 or 3) NPs with different compositions (Pd$_3$M, PdM, PdM$_3$) supported on carbon (Vulcan XC-72R) via solvothermal methodology which exhibit bifunctional activity toward ORR and oxygen evolution reactions (OER). The activity of the synthesized NPs was compared with the commercially available Pd/C and Pt/C catalyst. Scheme 5.1 shows the graphical representation of ORR as well as OER over the synthesized NPs.

This chapter is divided into three sections,

I. **Section 5A** Tuning the Electrocatalytic Activity of PdCu/C Nanoparticles toward Oxygen Reduction and Oxygen Evolution Reactions

II. **Section 5B** Composition Dependent Electrocatalytic Activity of PdNi/C Nanoparticles

III. **Section 5C** Synthesis and Characterization of PdCo/C Nanocatalysts and Their Electrochemical Activity
SECTION 5A: Tuning the Electrocatalytic Activity of PdCu/C Nanoparticles toward Oxygen Reduction and Oxygen Evolution Reactions

In this section of chapter 5 we have discussed about the development of carbon supported Pd$_x$Cu$_y$ bimetallic alloy nanoparticles and characterized by different spectroscopic and analytical techniques. The as-synthesized catalysts were found to be very effective and stable toward the electrochemical oxygen reduction as well as oxygen evolution reactions in alkaline medium.

5A.1 Results and Discussion

5A.1.1 Characterization of the synthesized PdCu/C nanoparticles

The structure and morphology of the synthesized Pd$_x$Cu$_y$/C NPs were investigated by means of X-ray diffraction (XRD), BET surface area analysis, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA), transmission and high resolution transmission electron microscopy (TEM-HRTEM) and X-ray photoelectron spectroscopy (XPS) techniques. Figure 5A.1 shows the XRD patterns of the as-synthesized PdCu$_3$/C, PdCu/C and Pd$_3$Cu/C nanoparticles.

![Figure 5A.1: X-ray diffraction pattern of Pd$_3$Cu/C, PdCu/C and PdCu$_3$/C NPs.](image)

From the XRD patterns it could be inferred that the PdCu NPs are well crystallized as four distinguished diffraction peaks can be observed. The first broad characteristic
diffraction peaks located at $2\theta = 24.8^\circ$ corresponds to (002) crystalline plane of carbon (JCPDS 75-1621). The other three diffraction peaks at $2\theta = 40.2$, 46.7, and 68.2 $^\circ$ could be indexed to the (111), (200) and (220) crystal planes of fcc type of Pd nanoparticles (JCPDS 88-2335) [33]. The diffraction peak at $2\theta = 40.2^\circ$ is slightly shifted to the higher diffraction angle in case of PdCu$_3$/C, i.e., with increasing the Cu content. Additionally, it is noted that the relative intensity of the peak at 40.2$^\circ$ gradually increases. Nevertheless the results revealed that the Pd diffraction peaks were slightly shifted to higher angles indicating the formation of carbon supported PdCu alloy NPs. No other additional peaks were detected signifying the high purity and good crystallinity of the samples. N$_2$ adsorption/desorption experiments was performed to investigate the surface and textural property of the synthesized nanoparticles. Figure 5A.2 represents the N$_2$ adsorption/desorption isotherms and BJH measurements (inset) for Pd$_3$Cu/C NPs. The isotherm represents type IV hysteresis loop of H3 type which signifies the mesoporous material. The BET surface area and the pore diameter are found to 30.1 m$^2$g$^{-1}$ and 3.22 nm, respectively.

![Figure 5A.2: N$_2$ adsorption desorption isotherm and the pore size distribution curve (inset) of Pd$_3$Cu/C.](image)

The EDX analysis shows the presence of detectable element Pd, Cu and C in the synthesized NPs (Figure 5A.3). The electron image and the EDX pattern are shown in the Figure 5A.3 (a,b), respectively. The EDS elemental maps for individual Pd, Cu and
C (Figure 5A.3 c-e) represent the spatial dissemination of the elements. No other elements were observed which confirms the purity of the sample. The bulk compositions of the obtained PdCu/C NPs were identified by ICP-OES analysis. The corresponding data are summarized in the Table 5A.1.

**Table 5A.1: ICP-OES results of the synthesized Pd$_x$Cu$_y$/C NPs.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd:Cu Molar concentration</th>
<th>Derived from ICP-OES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_3$Cu/C</td>
<td>3:1</td>
<td>0.76 : 0.24</td>
</tr>
<tr>
<td>PdCu/C</td>
<td>1:1</td>
<td>0.51 : 0.49</td>
</tr>
<tr>
<td>PdCu$_3$/C</td>
<td>1:3</td>
<td>0.23 : 0.77</td>
</tr>
</tbody>
</table>

The morphology of the synthesized NPs was further characterized by high resolution TEM (HRTEM) analysis. Figure 5A.4 (a-d) shows the TEM images of Pd$_3$Cu/C at
different resolutions. Homogeneous dispersion of the particles on the carbon support can be demonstrated from the TEM images. Although, we have recorded the TEM images of PdCu NPs without the carbon support it displays only some self-aggregated particles (Figure 5A.5). The stability of the synthesized NPs is significant as they are quite uniformly distributed on the carbon support evidenced from the respective TEM images (Figure 5A.4).

Figure 5A.4: (a)-(d) TEM images at different resolutions; the particle size distribution (inset image a), SAED pattern (inset image b) and the distinguished lattice fringes (inset image d) for Pd₃Cu/C NPs.

The size and the distribution of the particles were determined and found that most of the particles fall in the range of 3-5 nm with spherical morphology. Moreover the selected area diffraction (SAED) pattern represents well defined concentric rings which signify the polycrystallinity of the sample. The HRTEM image exhibits clear
lattice fringe as shown in the (inset image (Figure 5A.4d), the lattice spacing is found to be 0.21 nm which corresponds to the interplanar distance of (111) crystalline plane of fcc PdCu NPs.

Figure 5A.5: TEM images of Pd$_3$Cu nanoparticles without carbon support.

The chemical states of various elements of Pd$_3$Cu/C NPs, was investigated by X-ray photoelectron spectroscopy (XPS). Figure 5A.6(a) represents survey spectrum of the elements presents for Pd$_3$Cu/C. The high resolution C 1s XP spectrum (Figure 5A.6b) is deconvoluted into four different components at the binding energies of 284.9, 285.4, 286.6 and 289.3 eV which correspond to C–C (sp$^3$), C=C (sp$^2$), C–O and O=C–H species respectively [34, 35]. The peak intensity of C–C bond is quite strong which signify the presence of more sp$^3$-hybridized carbon in the synthesized NPs. The Pd 3d region shows predominantly two major peaks at the binding energy of 335.2 and 340.9 eV (Figure 5A.6c) which are attributed to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ species, respectively. After deconvolution it shows two additional peaks at the binding energies of 336.9 and 341.6 eV corresponding to Pd$^{2+}$ species. However, Pd is present mostly in the zero-valent state as the intensity of the peak at 335.2 eV is higher than that of the other. Figure 5A.6(d) displays the high resolution Cu 2p core-level XP spectrum.
Figure 5A.6: XPS analysis for Pd₃Cu/C NPs; (a) the survey spectrum and the high resolution core-level XP-spectrum of (b) C 1s, (c) Pd 3d and (d) Cu 2p region.

Two major peaks located at the binding energy of 932.3 and 952.1 eV which are ascribed to Cu 2p₃/2 and Cu 2p₁/2, respectively [36]. These two peaks are typically due to the zero-valent Cu. However, the deconvoluted spectrum shows two more additional peaks which are due to the Cu²⁺ species. Nevertheless, the results demonstrate the formation of Pd₃Cu/C NPs.

5A.1.2 Electrocatalytic activity of PdCu/C nanoparticles

The electrocatalytic activities of the as-prepared Pd₃Cuₓ/C towards ORR were examined using cyclic voltammetry (CV) and rotating disc electrode (RDE) measurements. Figure 5A.7 shows the CV plots of Pd₃Cu/C, PdCu/C and PdCuₓ/C respectively in 0.1 M KOH solution for both N₂ and O₂-saturated environment. An obvious and well-defined cathodic peak is observed in O₂ saturated KOH solution compared to that of N₂ which indicates good electrocatalytic activity of the catalyst towards ORR [37, 38]. As seen from the figure, Pd₃Cu/C shows ORR onset potential
of $\sim -0.37$ V (vs. Ag/AgCl) in N$_2$-saturated solution which is much more positively shifted, i.e., $\sim -0.26$ V (vs. Ag/AgCl) in O$_2$-saturated 0.1 M KOH solution. To get more insight on the catalytic activity for ORR, RDE measurements were performed at different rpm. Figure 5A.8 (a,c,e) shows the representative linear sweep voltammograms (LSVs) at the rotating rate of 400, 900, 1600, 2500 and 3600 rpm for Pd$_3$Cu/C, PdCu/C and PdCu$_3$/C, respectively.

On the basis of these ORR polarization curves, the number of electron transferred (n) in ORR is calculated according to Koutecky-Levich (K-L) equation.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B \omega^{0.5}}$$

$$B = 0.62 \times 10^{-5} \times 10^{2/3} \times 10^{1/6} \times 1.2 \times 10^6$$

Where, $j$ is the current density, $j_k$ is the kinetic current density, $\omega$ is the rotating rate of the electrode and B is the slope which could be obtained from the Koutecky-Levich plots. F is the Faraday constant (96500 C mol$^{-1}$), D$_{O_2}$ is the diffusion co-efficient of O$_2$ in 0.1 M KOH ($2.0 \times 10^{-5}$ cm$^2$ s$^{-1}$), $\nu$ is the kinetic viscosity (0.01 cm$^2$ s$^{-1}$), C$_{O_2}$ is the bulk concentration of O$_2$ (1.2 $\times$ 10$^{-6}$ mol cm$^{-3}$) and the value of ‘n’ represents the number of transferred electron in the ORR process. The K-L plots of $j^{-1}$ vs. $\omega^{1/2}$ at a potential of $-0.35$ V, $-0.40$ V, $-0.45$ V and $-0.50$ V displays good linearity (Figure 5A.8 b,d,f) which also indicates the first order kinetics of ORR.
From the slope values the ‘n’ value was calculated. At −0.40 V, ‘n’ is found to be 3.9 for Pd₃Cu/C, 3.84 for PdCu/C, and 3.6 for PdCu₃/C which are very close to 4.0. This implies that the ORR mechanism proceeds by “4e−” pathway (O₂ + 2H₂O + 4e− = 4OH⁻).

Figure 5A.8 Rotating rate dependent linear sweep voltammogram (LSVs) at the scan rate of 10 mVs⁻¹ in O₂-saturated 0.1 M KOH and the Koutecky-Levich plots of j¹ vs. ω⁻¹/² at different potential (a, b) for Pd₃Cu/C, (c, d) for PdCu/C and (e, f) for PdCu₃/C NPs.
Meanwhile the mass specific activities ($j_{\text{m}}$) are calculated at various potentials in the range of $-0.35 \text{ V}$ and $-0.50 \text{ V}$ for all the catalysts including the commercial Pd/C. Figure 5A.9(a) shows the plot of mass specific activities of those NPs at different potentials. Based upon the calculated value they follow the order $\text{Pd}_3\text{Cu/C} > \text{PdCu/C} > \text{PdCu}_3\text{/C}$. It should be mentioned that $\text{Pd}_3\text{Cu/C}$ possess almost two fold enhanced mass activity compared to that of commercial Pd/C. Moreover, the LSV plots for both $\text{Pd}_3\text{Cu/C}$ and commercial Pd/C at 1600 rpm is compared in the Figure 5A.9(b) from which it can be noticed that the synthesized catalyst exhibit lower ORR onset potential compared to that of the Pd/C. $\text{Pd}_3\text{Cu/C}$ shows ORR onset potential of $-0.07 \text{ V}$ which is much lower than that of Pd/C ($-0.12 \text{ V}$).

![Figure 5A.9:](image)

**Figure 5A.9:** (a) Mass specific activities of $\text{Pd}_3\text{Cu/C}$ NPs under different potential; (b) LSV curves at the rotating rate of 1600 rpm $\text{O}_2$-saturated 0.1 M KOH; (c) LSV curve after 1000 cycle to check the stability of $\text{Pd}_3\text{Cu/C}$ NPs and (d) LSVs of OER measurements.

The above results revealed that $\text{Pd}_3\text{Cu/C}$ NPs exhibited much higher electrocatalytic activity toward ORR. This finding may be attributed to the structural behavior of that particular composition which enhances the electrocatalytic performance toward ORR.
It follows an associative pathway/mechanism with the formation of *OOH intermediate which further dissociates to form O and OH [39]. It can be believed that for Pd₃Cu/C NPs the dissociation of *OOH, i.e., O–O bond dissociation is more favorable which efficiently raise the d-band center and hence enhance the electrocatalytic performance. It is predicted that ORR would be enhanced by coupling Cu, with low occupancy of d-orbitals with Pd possessing fully occupied d-orbitals [40]. Catalyst stability and durability is one of the major challenges in practical application. To study the stability of our catalyst we have performed LSV at 1600 rpm after 1000 reaction cycle. As shown in the Figure 5A.9(c), the Pd₃Cu/C shows very high catalytic stability as the difference of ΔE_{1/2} with the initial is quite low. This indicates that our synthesized catalyst has good recycling stability for ORR. Taking the excellent electrocatalytic activity, lastly we investigated their activity toward oxygen evolution reaction (OER) in 0.1 M KOH solution. Considerable efforts have been made to develop efficient electrocatalyst for OER in the last few years as it is play a vital role in many energy conversion and fuel cell application. Figure 5A.9 d displays the LSVs for OER in the potential window of 0.2 to 0.8 V vs. Ag/AgCl. Compared to the commercial Pd/C, Pd₃Cu/C exhibited high current nearly two fold greater and earliest onset potential which signifies the high electrocatalytic activity for OER. This excellent catalytic activity may be attributed to the well dispersion of the PdCu NPs on the carbon support which results in a novel heterogeneous structure with improved synergy of the two metals. Thus, these findings suggest that as-prepared Pd₃Cu/C NP is an efficient bifunctional electrocatalyst for ORR and OER.

In summary, a series of PdCu/C NPs were synthesized by modified solvothermal method with different compositions of Pd and Cu. Their electrocatalytic activity toward ORR in 0.1 M KOH solution were studied and Pd₃Cu/C showed best activity giving ‘n’ value 3.9 as the number of electron transferred. The mass specific activities are highly impressive and the catalyst is found to be quite stable after 1000 cycle. It is interesting to note that, they have tunable catalytic activity toward OER also in alkaline medium. Thus, the present investigation represents development of robust bifunctional electrocatalysts for ORR as well as OER in alkaline medium. The work offers an attractive strategy for the potential use in the future energy conversion technologies.
Section 5B: Composition Dependent Electrocatalytic Activity of PdNi/C Nanoparticles

In the section 5B different composition of carbon supported Pd$_x$Ni$_y$ bimetallic alloy nanoparticles were synthesized via solvothermal method and characterized them by various spectroscopic and analytical techniques. The electrocatalytic activities of the as-synthesized catalysts were evaluated for oxygen reduction and oxygen evolution reactions in alkaline medium.

5B.1 Results and Discussion

5B.1.1 Characterization of the synthesized Pd$_x$Ni$_y$/C nanoparticles

The as-synthesized Pd$_x$Ni$_y$/C NPs were first characterized by powder X-ray diffraction (XRD) analysis. The representative XRD pattern of the synthesized PdNi$_3$/C, PdNi/C and Pd$_3$Ni/C are shown in Figure 5B.1. The broad diffraction peak located at 2θ = 24.8° is corresponds to (002) crystalline plane of carbon according to the JCPDS 75-1621. The other three diffraction peaks at 2θ = 40.2, 46.7, and 68.2 ° could be indexed to the (111), (200) and (220) crystal planes of fcc type of Pd nanoparticles (JCPDS 88-2335).

![X-ray diffraction (XRD) pattern](image)

Figure 5B.1: X-ray diffraction (XRD) pattern of (a) PdNi$_3$/C; (b) PdNi/C and (c) Pd$_3$Ni/C NPs.
The diffraction peak at $2\theta = 44.4^\circ$ is corresponds to (111) crystalline plane of fcc lattice of cubic Ni nanoparticles according to the JCPDS 870712; which is much intense in case of PdNi/C (b) might be because of well crystallization of the two metals over this composition. However, the diffraction peaks of Pd are slightly shifted to the higher angles indicating the formation of carbon supported Pd$_3$Ni$_x$ alloy NPs. To investigate the surface and textural property we have carried out the N$_2$ adsorption/desorption experiments. Figure 5B.2 shows the N$_2$ adsorption/desorption isotherms and BJH measurements (inset) for Pd$_3$Ni/C NPs. From the isotherm type IV hysteresis loop of H3 is observed. The BET specific area is found to be $21.6 \text{ m}^2\text{g}^{-1}$. The pore diameter and the pore volume were calculated by using BJH method. The average pore diameter and pore volume are found to be 2.96 nm and 0.059 cc/g respectively. The pore diameter range suggests that the particles mesoporous in nature.

![Figure 5B.2: N$_2$ adsorption/desorption isotherm and the pore size distribution curve (inset) of Pd$_3$Ni/C NPs.](image)

To know the elements present in the synthesized catalyst, EDX analysis was carried out. Figure 5B.3 shows the EDX pattern along with the EDS elemental maps for individual Pd, Ni and C respectively. The presence of the only detectable element Pd, Ni and C in the synthesized NPs signify the high purity of the sample. The elemental maps show how the particles are distributed on the catalyst surface.
Figure 5B.3: EDX analysis of Pd$_3$Ni/C nanoparticles (a) the electron image (b) the EDX pattern and (c)-(e) elemental maps for individual Pd, Ni and C, respectively.

Figure 5B.4: (a)-(d) TEM images at different resolution; (e) the SAED pattern and (f) the particle size distribution for Pd$_3$Ni/C NPs.
The morphology of the synthesized NPs was characterized by high resolution TEM (HRTEM) analysis. The representative TEM images of Pd$_3$Ni/C at different resolutions are presented in the Figure 5B.4. From these images, it is observed that the small metallic nanoparticles are quite homogeneously distributed on the carbon support. Most of the particles spherical in in nature which is clearly seen from image (d). It can be specified that, over the carbon support the metallic PdNi nanoparticles are stabilized giving less agglomeration unlike the unsupported ones. Figure 5B.4 (e) shows the selected area diffraction (SAED) pattern, which represents well defined concentric rings. From this observation, the polycrystallinity of the synthesized NPs are established. Moreover, the size and the distribution of the particles were also determined by using Image J software and plotted in a histogram as shown in Figure 5B.4 (f). Most of the metallic nanoparticles are < 8 nm in size with an average size of 4.2 nm.

To investigate the chemical states of various elements present X-ray photoelectron spectroscopy (XPS) were further employed. The XPS analysis of the Pd$_3$Ni/C NPs is shown in Figure 5B.5. The survey spectrum (a) displays the presence of Pd, Ni and C in the synthesized catalyst. Figure 5B.5 (b) represents the high resolution C 1s XP spectrum with four different components. The most intense peak at the binding energies of 284.9 eV is corresponds to sp$^3$ hybridized C–C species. Other three peaks at the binding energies of 285.4, 286.6 and 289.3 eV are related to C=C (sp$^2$), C–O and O=C–H species respectively. The core- level Pd 3d XP spectrum is shown in Figure 5B.5 (c). The two major peaks at the binding energy of 335.2 and 340.9 eV correspond to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ species respectively. This indicates that Pd species are mostly zero valent. However, after deconvolution two more additional peaks are observed at the binding energies of 336.9 and 341.6 eV corresponds to Pd$^{2+}$ species. Figure 5B.5 (d) shows the core-level XP spectrum of Ni 2p. Two major peaks at the binding energy of 856.4 and 873.4 eV are corresponds to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$, respectively [41, 42]. Together with them two more satellite peaks at the binding energy of 861.2 and 879.9 eV are also observed which are basically due to the presence of Ni$^{2+}$ species in the synthesized catalyst. Nevertheless the result demonstrates the formation of carbon supported bimetallic PdNi nanoparticles.
Figure 5B.5: XPS analysis for Pd$_3$Ni/C NPs (a) the survey spectrum; and the high resolution core-level XP-spectrum of (b) C 1s, (c) Pd 3d and (d) Ni 2p region.

5B.1.2 Electrocatalytic activity of PdNi/C nanoparticles

The electrocatalytic activities towards ORR of the Pd$_x$Ni$_y$/C NPs studied by using cyclic voltammetry (CV) and rotating disc electrode (RDE) measurements. The CV plots in 0.1 M KOH solution for both N$_2$ and O$_2$-saturated environment of Pd$_3$Ni/C, PdNi/C and PdNi$_3$/C are shown in the Figure 5B.6(a-c), respectively. From the CV plots, strong, much intense cathodic peaks are observed with high current density for O$_2$ saturated KOH solution compared to that of N$_2$. This suggests that the catalysts have good electrocatalytic activity of towards ORR. The ORR activity further investigated by RDE measurements performed at different rpm. The linear sweep voltammogram (LSVs) for the different catalysts were recorded at the rotating rate of 400, 900, 1600, 2500 and 3600 rpm. The representative LSVs for Pd$_3$Ni/C, PdNi/C and PdNi$_3$/C are shown in the Figure 5B.7 (a), (c) and (e) respectively.
The number of electron transferred (n) in ORR is calculated according to Koutecky-Levich (K-L) equation on the basis of these ORR curves as mentioned in the section 5A. The linear plots of \( j^{-1} \) vs. \( \omega^{-1/2} \) at a potential of \(-0.40 \) V displays good linearity for all the composition of Pd\(_x\)Ni\(_y\)/C NPs. Figure 5B.7 (b), (d) and (f) represents the K-L plots of Pd\(_x\)Ni\(_y\)/C, PdNi/C and PdNi\(_y\)/C NPs respectively. The first order kinetics of ORR can be recognized from this observation. From the slope of K-L plots the values the ‘n’ value calculated and found to be 4.01 for Pd\(_x\)Ni\(_y\)/C, 3.9 for PdNi/C, and 3.7 for PdNi\(_y\)/C which are very close to 4.0. This implies that the ORR mechanism proceeds by “4e\(^-\)” pathway. To compare the electrocatalytic activity of Pd\(_x\)Ni\(_y\)/C with commercial Pt/C and Pd/C, we have recorded their LSVs at 1600 rpm. Figure 5B.8 (a) shows the LSVs plots of the same. The onset potential and the current density at 1600 rpm of the catalysts are summarized in the Table 5B.1.
Figure 5B.7: Rotating rate dependent linear sweep voltammogram (LSVs) at the scan rate of 10 mVs$^{-1}$ in O$_2$-saturated 0.1 M KOH and the Koutecky-Levich plots of $j^{-1}$ vs. $\omega^{-1/2}$ at different potential for Pd$_3$Ni/C (a, b); PdNi/C (c, d) and PdNi$_3$/C (e, f) NPs respectively.
Table 5B.1: Summary of onset potential and current density over different catalysts towards ORR at 1600 rpm

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset potential (V)</th>
<th>Current density (j/mAcm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Pd/C</td>
<td>−0.12</td>
<td>−2.4</td>
</tr>
<tr>
<td>Commercial Pt/C</td>
<td>−0.08</td>
<td>−3.7</td>
</tr>
<tr>
<td>Pd₃Ni/C</td>
<td>−0.04</td>
<td>−4.9</td>
</tr>
</tbody>
</table>

Figure 5B.8: (a) LSV curves at the rotating rate of 1600 rpm O₂-saturated 0.1 M KOH; (b) Mass specific activities under different potential; (c) LSVs of OER measurements.

Compared to the commercial Pd/C and Pt/C, the synthesized Pd₃Ni/C NPs exhibited much lower onset potential and high current density for ORR. This observation indicates that the synthesized nanocatalyst can efficiently favors the electrochemical
oxygen reduction reaction in alkaline medium. The mass activity of the synthesized NPs, mass specific activities ($j_m$) were calculated at four different potential; $-0.35$ V, $-0.40$ V, $-0.45$ V and $-0.50$ V along with the commercially available Pd/C. Figure 5B.8 (b) shows the plot of mass specific activities of those NPs at different potentials. Among all the catalyst, Pd$_3$Ni/C possesses higher mass activity toward ORR. They follow the order Pd$_3$Ni/C $>$ PdNi/C $>$ PdNi$_3$/C. Lastly, the electrocatalytic activity toward oxygen evolution reaction (OER) in 0.1 M KOH solution was also investigated for Pd$_3$Ni/C NPs. Figure 5B.8 (c) displays the LSVs for OER in the potential window of 0.2 to 0.8 V vs. Ag/AgCl. Compared to the commercial Pd/C, Pd$_3$Ni/C exhibited high current and lower onset potential which signifies the high electrocatalytic activity for OER. These findings revealed that as-prepared carbon supported bimetallic PdNi alloy nanoparticles are efficient electrocatalyst for electrochemical oxygen reduction and oxygen evolution reactions.

In conclusion, a series of Pd$_x$Ni$_y$/C NPs were synthesized by modified Solvothermal method. The catalysts were found to be very effective toward ORR as well as OER in alkaline medium. The transfer of electron in ORR is found to be $\sim 4$ for all three compositions of Pd$_x$Ni$_y$/C NPs. This suggests that the ORR mechanism follows 4e$^-$ pathway. The activity is compared with that of the commercially available Pt/C and Pd/C. Thus, the present investigation proposes a noteworthy application of Pd$_x$Ni$_y$/C NPs in the fields of fuel cell reactions.
SECTION 5C: Synthesis and Characterization of PdCo/C Nanocatalysts and Their Electrochemical Activity

In this section of chapter 5; different composition of PdCo/C nanocatalysts were synthesized and characterized by different spectroscopic and analytical techniques. Their electrochemical activities were investigated for the oxygen reduction and oxygen evolution reactions in alkaline medium.

5C.1 Results and Discussion

5C.1.1 Characterization of the synthesized PdCo/C nanoparticles

The as-synthesized different compositions of PdCo/C NPs were first characterized by powder X-ray diffraction (XRD) analysis. Furthermore, they were also characterized by other analytical and spectroscopic techniques such as BET surface area analysis, inductively coupled plasma-optical emission spectrometer (ICP-OES), energy dispersive X-ray analysis (EDXA), transmission and high resolution transmission electron microscopy (TEM-HRTEM) and X-ray photoelectron spectroscopy (XPS) techniques.

![X-ray diffraction pattern of Pd₃Co/C, PdCo/C and PdCo₃/C NPs](image)

**Figure 5C. 1:** X-ray diffraction pattern of Pd₃Co/C, PdCo/C and PdCo₃/C NPs

Figure 5C.1 shows the XRD patterns of the as-synthesized PdCo₃/C, PdCo/C and Pd₃Co/C nanoparticles. The most intense peaks at the diffraction angle 2θ = 40.2, 46.7, and 68.2° are corresponds to the (111), (200) and (220) crystal planes of fcc type of Pd
nanoparticles (JCPDS 88-2335). The broad peak located at 2θ = 24.8° is corresponds to (002) crystalline plane of carbon according to the JCPDS 75-1621. The intensity of the characteristic diffraction peak at 2θ = 40.2° is slightly lower in case of PdCo/C i.e. with decreasing the Pd content. Nevertheless, like the other systems that we have already discussed in the section 5A and 5B; these results also revealed the formation of carbon supported PdCo bimetallic NPs. No other additional peaks were detected signifying the high purity and good crystallinity of the sample. Furthermore, the Pd₃Co/C NPs were characterized by N₂ adsorption/desorption experiments performed at -196 °C. Figure 5C.2 represents the N₂ adsorption/desorption isotherms and BJH measurements (inset) for Pd₃Co/C NPs. A type IV hysteresis loop of H3 isotherm is observed for Pd₃Co/C which signifies the mesoporous material. The BET specific surface area and the pore diameter of the NPs are found to 75.8 m²g⁻¹ and 7.07 nm respectively.

![N₂ adsorption desorption isotherm and the pore size distribution curve (inset) of Pd₃Co/C NPs.](image)

**Figure 5C.2:** N₂ adsorption desorption isotherm and the pore size distribution curve (inset) of Pd₃Co/C NPs.

The EDX analysis was performed to investigate the presence of detectable element i.e. Pd, Co and C in the synthesized NPs. Figure 5C.3 shows the electron image along with the EDX pattern and EDS elemental maps for Pd, Co and C respectively. No other elements were observed which confirms the purity of the sample. Moreover, ICP-OES
analysis was also done to know the bulk compositions of the obtained PdCo/C NPs. The corresponding ICP-OES data are summarized in the Table 5C.1.

Table 5C.1: ICP-OES results of the synthesized Pd₃Co/C NPs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd:Co Molar concentration</th>
<th>Derived from ICP-OES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₃Co/C</td>
<td>3:1</td>
<td>0.76 : 0.24</td>
</tr>
<tr>
<td>PdCo/C</td>
<td>1:1</td>
<td>0.51 : 0.49</td>
</tr>
<tr>
<td>PdCo₃/C</td>
<td>1:3</td>
<td>0.23 : 0.77</td>
</tr>
</tbody>
</table>

The morphology of the synthesized NPs was characterized by high resolution TEM (HRTEM) analysis. The representative TEM images of Pd₃Co/C at different resolutions are shown in Figure 5C.4. The particles are homogeneously dispersed on the carbon support which can be inferred from the TEM images. From this
observation, we can say that the use of carbon as a support could stabilize the small aggregates to some extent.

![Image](image1.png)

**Figure 5C.4:** (a)-(d) TEM images at different resolution; the SAED pattern (inset image b), the particle size distribution (inset image c) for PdCo/C NPs.

The selected area diffraction (SAED) pattern (inset image b) represents well defined concentric rings as the earlier cases, which signify the polycrystallinity of the sample. Using Image J; the size and the distribution of the particles were determined and found that most of the particles are < 6 nm with spherical morphology.

X-ray photoelectron spectroscopy (XPS) was used to study chemical states of the existing elements of the synthesized catalyst. The XPS analysis for PdCo/C NPs is demonstrated in the Figure 5C.5. The survey spectrum shows the presence of C 1s, Pd 3d and Co 2p in the synthesized catalyst. The high resolution C1s XP spectrum (Figure 5C.5 b) predominantly shows the major peak at the binding energy of 284.9 eV that
correspond to sp$^3$ hybridized C–C bond. After deconvolution, C–O component is also observed at the binding energies of 286.6 eV. As similar to the earlier cases, Pd 3d region shows predominantly two major peaks at the binding energy of 335.2 and 340.9 eV (Figure 5C.5 c) which corresponds to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ species respectively. After deconvolution it shows two additional peaks at the binding energies of 336.9 and 341.6 eV further demonstrate the formation of Pd$^{2+}$ species.

![Figure 5C.5: XPS analysis for Pd$_3$Co/C NPs (a) the survey spectrum; and the high resolution core-level XP-spectrum of (b) C 1s, (c) Pd 3d and (d) Co 2p region.](image)

However, Pd is present mostly in the zero-valent state as the intensity of the peak at 335.2 eV is higher than that of the other. The core-level Co 2p XP spectrum is shown in the Figure 5C.5 (d). Two predominant peaks at the binding energy of 782.1 and 796.0 eV are detected. These two peaks are correspond to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively [43, 44]. Together with them, two more “shake-up” satellite peaks (represented as Sat.) at the binding energies of 785.6 and 803.5 eV are also observed.
The satellite peaks demonstrate the co-existence of Co$^{2+}$ species in the catalyst. Nevertheless, the results demonstrate the formation of Pd$_3$Co/C NPs.

5C.1.2 Electrocatalytic activity of PdCo/C nanoparticles

The electrocatalytic activities of the as-prepared Pd$_3$Co$_y$/C towards ORR in alkaline medium were examined using cyclic voltammetry (CV) and rotating disc electrode (RDE) measurements. We have recorded the CV for 0.1 M KOH solution for both N$_2$ and O$_2$-saturated environment. The CV plots of Pd$_3$Co/C NPs are shown in the Figure 5C.6 (a). The peak is shifted to right i.e. positively shifted with high current density in O$_2$ saturated KOH solution compared to that of N$_2$ which indicates good electrocatalytic activity of the catalyst towards ORR.

Figure 5C.6: (a) Cyclic voltammetry (CV) plots in both N$_2$ and O$_2$-saturated 0.1 M KOH solution (b) LSVs at the scan rate of 10 mVs$^{-1}$ at different rotating rate (c) K-L plots at different potential and (d) plot of the number of electron transferred in ORR for Pd$_3$Co/C NPs.
The ORR was further investigated by RDE measurements at different rotating rate. Figure 5C.6(b) represents the linear sweep voltammogram (LSV) at five different rotating rates for ORR. On the basis of these ORR polarization curves, using Koutecky-Levich (K-L) equation already mentioned in the section 5A the number of electron transferred (n) in ORR was calculated. The K-L plots of j\(^{-1}\) vs. \(\omega^{-1/2}\) at a potential of −0.35 V, −0.40 V, −0.45 V and −0.50 V displays good linearity (Figure 5C.6 c) which also indicates the first order kinetics of ORR. From the slope values the ‘n’ value was calculated. At all potentials, the value of ‘n’ are found to be very close to 4.0. In the Figure 5C.6 (d) we have plotted the transfer of electron number at different potential for ORR using Pd\(_3\)Co/C NPs. From this we can conclude that, the reaction is proceeds by “4e\(^-\)” pathway, i.e., \(\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-\) (alkaline medium).

Figure 5C.7: Rotating rate dependent linear sweep voltammogram (LSVs) at the scan rate of 10 mVs\(^{-1}\) in O\(_2\)-saturated 0.1 M KOH and Koutecky-Levich (K-L) plots of j\(^{-1}\) vs. \(\omega^{-1/2}\) for ORR using (a, b) PdCo/C and (c, d) PdCo\(_3\)/C NPs, respectively.
Figure 5C.7 (a) and (b) shows the rotating rate dependent LSVs at the scan rate of 10 mVs\(^{-1}\) in O\(_2\)-saturated 0.1 M KOH and the K-L plots of \(j^{-1}\) vs. \(\omega^{-1/2}\) (inset) for PdCo/C and PdCo\(_3\)/C NPs respectively. The transfer of electron number was calculated and found to be 4.18 and 3.5 for PdCo/C and PdCo\(_3\)/C NPs respectively. Thus, it can be stated that, the carbon supported PdCo bimetallic NPs can efficiently catalyze the electrochemical oxygen reduction reaction in alkaline medium. The present investigation thus signifies a notable approach to design PdCo alloy NPs on carbon support for the applications of electrochemical reactions in fuel cells. However, to compare the activity of our synthesized catalysts with the commercial Pt/C and Pd/C; LSVs were recorded at 1600 rpm. Figure 5C.8 (a) shows the LSV plots of the same. We have summarized the onset potential and current density for this investigation in the Table 5C.2.

**Table 5C.2: Summary of onset potential and current density over different catalysts towards ORR at 1600 rpm**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset potential (V)</th>
<th>Current density (j/mAcm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Pd/C</td>
<td>−0.12</td>
<td>−2.4</td>
</tr>
<tr>
<td>Commercial Pt/C</td>
<td>−0.08</td>
<td>−3.7</td>
</tr>
<tr>
<td>Pd(_3)Co/C</td>
<td>−0.02</td>
<td>−6.4</td>
</tr>
</tbody>
</table>

The improved electrocatalytic activity of the Pd\(_3\)Co/C NPs may be attributed to their distinctive structural behavior which makes the dissociation of *OOH intermediate during ORR much promising. We have also investigated their mass specific activities (\(j_m\)) at different potentials in the range of −0.35 V and −0.50 V for all the catalysts and compared the data with commercial Pd/C. Figure 5C.8 (b) shows the plot of mass specific activities of those NPs at different potentials. Based upon the calculated value they follow the order Pd\(_3\)Co/C > PdCo/C > PdCo\(_3\)/C > commercial Pd/C. It should be mentioned that Pd\(_3\)Co/C and PdCo/C NPs possess almost similar mass activity. To investigate the catalyst stability we have performed LSV at 1600 rpm after 1000 reaction cycle. As shown in the Figure 5C.8 (c), the Pd\(_3\)Co/C show very high catalytic stability and durability as the difference of \(\Delta E_{1/2}\) with the initial is quite low which makes them practically viable in use. This indicates that our synthesized catalyst has...
good recycling stability for ORR. Taking the excellent electrocatalytic activity, lastly we investigated their activity toward oxygen evolution reaction (OER); that play a vital role in many energy conversion and fuel cell application. We have investigated their OER activity in 0.1 M KOH solution in the potential window of 0.2 to 0.8 V vs. Ag/AgCl. Figure 5C.8 (d) displays the LSVs for OER which is compared with the commercial Pd/C. Pd₃Co/C exhibited high current and earliest onset potential which signifies the high electrocatalytic activity for OER.

![Figure 5C.8](image)

**Figure 5C.8:** (a) LSV curves at the roatating rate of 1600 rpm O₂-saturated 0.1 M KOH; (b) Mass specific activities of Pd₃Co/C NPs under different potential; (c) LSV curve after 1000 cycle to check the stability of Pd₃Co/C NPs and (d) LSVs of OER measurements.

In summary, a series of PdCo/C NPs were successfully synthesized via solvothermal method with different compositions of Pd and Co. The catalysts exhibited enhanced electrocatalytic activity toward ORR in 0.1 M KOH solution. Pd₃Co/C NPs have long-term stability toward ORR. Thus, the work affords an efficient and facile route for the development of bifunctional electrocatalysts for ORR as well as OER in alkaline medium.
REFERENCES


