Graphene-supported Palladium and (40-x)wt% Pd-xwt%Co (0 ≤ x ≤ 13.33) composites were prepared by a polyol reduction method and investigated for their physicochemical and electrocatalytic properties for use as methanol tolerant electrocatalysts for the ORR in an acid medium. All the composites prepared have been found to be active for ORR and inactive for MOR. Results of the investigation are fully described in the present section.

4.4.1 Structural characterization

4.4.1.1 X-ray Diffraction (XRD)

The XRD patterns of the composite, 40wt%Pd/GNS and (40-x)wt%Pd-x wt%Co(0 ≤ x ≤ 13.33) are recorded between 2θ = 20 and 2θ = 80° and the same are reproduced in Fig.4.4.1. The XRD pattern of all the composites show the three diffraction peaks of Pd at 2θ ≈ 40°, 46.5° and 68.2°, which correspond to planes (111), (200) and (220), respectively. These peaks are characteristics of the face-centered-cubic (fcc) crystalline Pd structure (Singh et al., 2011b; Zhao et al., 2011). The broad peak invariably observed between 2θ = 24 and 26° in all the XRD patterns can be attributed to the graphene support (Yang et al., 2013; Singh et al., 2011b).

The observation of Fig.4.4.1 further shows that all the diffraction peaks for the Pd-Co/GNS bimetallic composites are shifted slightly towards the higher 2θ(with respect to the corresponding peaks in the Pd/GNS composite), magnitude of shift in 2θ values being 0.5-1° with 3.6 - 13.3 wt% Co addition in the composite. This small shift in 2θ values reveals an alloy formation between Pd and Co and indicates a lattice contraction, which are caused by the incorporation of Co into the Pd fcc structure. Although no reflections for pure Co and its oxides are found, their presence may not be completely ruled out due to their smaller concentration level and possibly poor crystallinity.
The lattice parameter ($\delta$) and the mean crystallite size ($S$) of Pd nanoparticles in all the four catalysts have also been determined. The most intense diffraction peak of Pd corresponding to the plane (111) was employed to determine the Pd crystallite sizes ($S$) by using Scherrer formula. The lattice parameter was calculated by using the equation (7)

$$\sin^2 \theta = \frac{\lambda^2}{4\delta^2} (h^2 + k^2 + q^2)$$ .................................. (7)

where $\lambda$ is the CuK\(\alpha\) radiation wave length, 1.5418 Å, $\delta$ is the lattice parameter and h,k,q are the lattice index parameters (Mustain et al., 2007). Estimates of $S$ and $\delta$ for Pd in 40wt% Pd/GNS, 36.36wt% Pd 3.64wt% Co/GNS, 32wt% Pd 8wt% Co/GNS and 26.27wt% Pd 13.33wt% Co/GNS composites are given in Table 4.4.1. Thus, results show that as the Co content increases in the Pd-Co alloy, both the mean crystallite size (Wang et al., 2007; Li et al., 2008) and the lattice parameters (Wang et al., 2007; Mustain et al., 2007) decrease. The decrease in value of the lattice parameter might result from a lattice contraction upon alloying (Wang et al., 2007).

**Table 4.4.1:** Values of the cell parameters and crystallite size.

<table>
<thead>
<tr>
<th>Composites</th>
<th>XRD Analysis for (111) plane</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lattice Parameter (Å)</td>
<td>Pd-Pd bond distance (Å)</td>
</tr>
<tr>
<td>40wt % Pd/GNS</td>
<td>0.390</td>
<td>2.2513</td>
</tr>
<tr>
<td>36.36wt % Pd 3.64wt % Co/GNS</td>
<td>0.389</td>
<td>2.2458</td>
</tr>
<tr>
<td>32wt % Pd 8wt % Co/GNS</td>
<td>0.387</td>
<td>2.2343</td>
</tr>
<tr>
<td>26.27wt% Pd 13.33wt% Co/GNS</td>
<td>0.385</td>
<td>2.2227</td>
</tr>
</tbody>
</table>

Fig. 4.4.1: XRD patterns of Pd/GNS and Pd-Co/GNS composites
4.4.1.2 TEM

Fig. 4.4.2 (a-f) shows TEM images of composites, 40wt% Pd/GNS, 26.67wt% Pd 13.33wt% Co/GNS and 32wt% Pd 8wt% Co/GNS. These figures show good dispersion of Pd and Pd-Co nanoparticles (NPs) on GNS. However, at some regions, the NPs appear to be concentrated which may be caused due to the presence of considerable number of functional groups on the GNS surface (Choi et al., 2011). Some dark contrast within the pictures are also seen which probably may be due to Bragg orientation of metal particles. There is also possibility of over deposition of metal NPs which may cause mass contrast. The average particles size estimated, based on the observation of more than 100 particles on TEM pictures of 40wt % Pd/GNS, 26.67wt % Pd 13.33wt % Co/GNS and 32wt % Pd 8wt % Co/GNS composites are listed in Table 4.4.1. Values of the crystallite size obtained from TEM pictures are close to ones obtained from the XRD study.

![TEM images of composites](image)

**Fig. 4.4.2:** TEM images of 40wt % Pd/GNS (a and b), 26.67wt % Pd 13.33wt % Co/GNS (c and d) and 32wt % Pd 8wt % Co/GNS (e and f).
4.4.2 Electrochemical characterization

4.4.2.1 Cyclic voltammetry (CV)

Figs. 4.4.3 (A&B) and 4.4.4 gather CVs of 30wt%Pd/GNS, 40wt%Pd/GNS and 50 wt%Pd/GNS and (40-x) wt% Pdx wt% Co/GNS (0 ≤ x ≤ 13.33) composites, recorded at the scan rate (v) of 50 mV s⁻¹ in the potential region from -0.058 to +1.542 V vs. RHE in Ar-saturated 0.5 M H₂SO₄ and 0.5 M H₂SO₄ + 1M CH₃OH, at 25°C. Features of curves shown in Figs. 4.4.3 (A&B) and 4.4.4 are similar, regardless of the nature of the electrode and electrolyte. The oxidation-reduction peaks observed in the potential region, from 0.342 to -0.058 V vs RHE, are produced due to the adsorption / desorption of hydrogen (Salvador-Pascual et al., 2007). The wave-like shape of voltammograms on the positive-going scan and prior to the commencement of the O₂ evolution reaction (OER) can be ascribed to a slow electrochemical oxidation of the palladium surface into palladium (II) oxide (Madhu et al., 2011). A relatively strong cathodic peak observed at E = 0.556-0.615 V vs. RHE on the negative-going scan is caused due to the reduction of palladium (II) oxide, formed under anodic condition, into palladium metal (Singh et al., 2011b; Zhao et al., 2011; Mustain et al., 2007; Pattabiraman et al., 1997). The relatively larger anodic peak, observed in the potential range between -0.058 V and 0.342 V vs. RHE, for the Pd-Co/GNS catalyst in comparison with those for Pd-Co/GNS (base catalyst, Fig. 4.4.3 B) might indicate the dissolution of adsorbed hydrogen into bulk Pd. The addition of Co within the catalyst might restrain dissolution of hydrogen into bulk Pd-Co/GNS as compared to pure Pd catalyst (Lee et al., 2006).
Fig. 4.4.3: Cyclic Voltammograms of 30wt%Pd/GNS, 40wt%Pd/GNS and 50wt%Pd/GNS (A) and Pd-Co/GNS (B) composites in Ar-saturated 0.5 M H₂SO₄. Scan rate = 50 mVs⁻¹ and T = 25°C.

As discussed in section 4.1 and 4.2, the EASA of the composite was estimated by determining the coulombic charge (Q/mC) for the reduction of palladium oxide (Awasthi et al., 2012; Pattabiraman et al., 1997) and using the relation, EASA = Q (mC)/S (mC cm⁻²), The EASA values of catalysts (in ‘cm²’), thus estimated, are listed in Table 4.4.2.

Table 4.4.2: Electrocatalytic properties of (40-x)wt% Pd x wt% Co nanoparticles dispersed on GNS in 0.5 M H₂SO₄; geometrical area of the electrode = 0.5 cm²; metal loading (l) = 0.12 mg cm⁻², T= 25°C.

<table>
<thead>
<tr>
<th>x / wt%</th>
<th>10⁻³×l / mg cm⁻²</th>
<th>Q / mC</th>
<th>EASA</th>
<th>Apparent current at E = 0.442 V /</th>
<th>10⁻⁴× Specific activity / mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Co</td>
<td></td>
<td></td>
<td>cm⁻²</td>
<td>cm⁻² mg⁻¹_pdm</td>
</tr>
<tr>
<td>0</td>
<td>9</td>
<td>0</td>
<td>11</td>
<td>27.2</td>
<td>604</td>
</tr>
<tr>
<td>0</td>
<td>12</td>
<td>0</td>
<td>16</td>
<td>39.5</td>
<td>658</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
<td>0</td>
<td>13</td>
<td>32.1</td>
<td>428</td>
</tr>
<tr>
<td>3.64</td>
<td>10.9</td>
<td>1.1</td>
<td>18</td>
<td>44.4</td>
<td>823</td>
</tr>
<tr>
<td>5.72</td>
<td>10.3</td>
<td>1.7</td>
<td>19</td>
<td>46.9</td>
<td>920</td>
</tr>
<tr>
<td>8.00</td>
<td>9.6</td>
<td>2.4</td>
<td>23</td>
<td>56.8</td>
<td>1183</td>
</tr>
<tr>
<td>13.33</td>
<td>8.0</td>
<td>4.0</td>
<td>6</td>
<td>14.8</td>
<td>380</td>
</tr>
</tbody>
</table>

From the table it is also clear that addition of Co into Pd/GNS increases the EASA up to 8wt% and diminishes thereafter (i.e. 13.33 wt%Co). The observed EASA of a particular electrocatalyst has also been normalized with respect to the actual Pd mass taken in that
electrocatalyst assuming the contribution of the entire Pd mass to the EASA. Based on values of the EASA per mg of Pd, the catalysts investigated follow the order:

\[
32\text{wt}\% \text{Pd 8wt}\% \text{Co/GNS} > 34.28\text{wt}\% \text{Pd 5.72wt}\% \text{Co/GNS} > 36.36\text{wt}\% \text{Pd 3.64wt}\% \text{Co/GNS} > 40\text{wt}\% \text{Pd/GNS} > 50\text{wt}\% \text{Pd/GNS} > 30\text{wt}\% \text{Pd/GNS} > 26.67\text{wt}\% \text{Pd13.33}\% \text{Co/GNS}.
\]

Features of CVs of Pd-Co/GNS composites recorded in Ar-saturated 0.5 M H$_2$SO$_4$ containing 1 M CH$_3$OH shown in Fig. 4.4.4 are also similar to those recorded in absence of methanol under similar experimental conditions (Fig.4.4.3 A&B); they do not show any characteristic current peak for the alcohol oxidation. Thus, results show that Pd-Co bimetallic composites are perfectly immune to the MOR in acid solutions and can be used as methanol tolerant oxygen reduction electrocatalysts.

![Cyclic Voltammograms of Pd/GNS and PdCo/GNS composites in Ar saturated 0.5 M H$_2$SO$_4$ + 1 M CH$_3$OH. Scan rate = 50 mVs$^{-1}$ & T = 25°C.](image)

Fig.4.4.4: Cyclic Voltammograms of Pd/GNS and PdCo/GNS composites in Ar saturated 0.5 M H$_2$SO$_4$ + 1 M CH$_3$OH. Scan rate = 50 mVs$^{-1}$ & T = 25°C.

### 4.4.2.2 Electrocatalytic activity: LSV

Fig.4.4.5 A & B shows the Linear sweep voltammietries (LSVs) of 30wt%Pd/GNS, 40wt%Pd/GNS, 50wt%Pd/GNS and (40-x) wt% Pd xwt% Co/GNS (0 ≤ x ≤ 13.33) composites recorded in the potential region from + 0.842 to + 0.042 V vs. RHE at the scan rate (v) of 5 mV s$^{-1}$ in Ar- and O$_2$-saturated 0.5 M H$_2$SO$_4$ at 25°C. The LSV curves shown in Fig.4.4.5A show that the composite, 40wt%Pd/GNS shows superior ORR performance over 30wt%Pd/GNS and 50wt%Pd/GNS.
LSVs of electrocatalysts in Ar-saturated 0.5 M \( \text{H}_2\text{SO}_4 \) were similar and seem to have very little (i.e. negligible) current contributions towards the electroreduction of oxygen. A typical LSV curve for the 32 % Pd 8 % Co/GNS catalyst in Ar-saturated 0.5 M \( \text{H}_2\text{SO}_4 \) is shown in Fig.4.4.5 B. However, LSV curves recorded in \( \text{O}_2 \)-saturated solution as shown in Fig.4.4.5B exhibit that the electrode materials investigated are ORR active and that among the bimetallic Pd-Co composites, the 32wt% Pd 8wt % Co/GNS electrode is the greatest ORR active while that the 26.67wt % Pd 13.33wt % Co electrode is the least ORR active. Based on ORR current densities at a constant potential, \( E = 0.442 \text{ V vs. RHE} \), The catalyst electrodes can be placed in the activity order: 32wt % Pd 8wt % Co/GNS (1.58 mA cm\(^{-2}\)) > 34.28wt % Pd 5.72wt % Co/GNS (1.42 mA cm\(^{-2}\)) > 36.36wt % Pd 3.64wt % Co/GNS (1.06 mA cm\(^{-2}\)) > 26.67wt % Pd 13.33wt % Co/GNS (0.84 mA cm\(^{-2}\)) > 40wt % Pd/GNS (0.66 mA cm\(^{-2}\)) > 50wt % Pd/GNS (0.50 mA cm\(^{-2}\)) > 30wt % Pd/GNS (0.34 mA cm\(^{-2}\)).
Fig. 4.4.5: Linear Scan Voltammograms of 30wt%Pd/GNS, 40wt%Pd/GNS and 50wt%Pd/GNS (A) and PdCo/GNS (B) composites in O₂-saturated 0.5 M H₂SO₄. Scan rate = 5 mVs⁻¹ & T = 25°C.

On the basis of above results, it can concluded that the enhanced catalytic activities for Pd-Co composites in comparison with pure Pd may be attributed to the alloying of Pd and Co followed by a lattice compression (i.e. reduction in Pd-Co bond). The lattice compression results in shift of d-band center, which has an effect on surface activity of Pd sites. It has already been shown by DFT calculation that the compression of a Pd lattice in alloy produces the downshift of the d-band center energy (Hammer et al., 2000). The increase in the specific activity of the electrode with Co introduction for Pd shown in Table 4.4.2 also indicates modification in the electronic properties of the electrode material in favour of electrocatalysis of the ORR. The decrease in the apparent ORR activity at the higher Co addition (13.33%) can be ascribed to somewhat lowering of percentage of Pd in the bimetallic alloy. Also, blocking of some active Pd sites at higher Co additions cannot be ruled out.

Fig. 4.4.6: Linear Scan Voltammograms of 32wt% Pd 8wt% Co supported on GNS and MWCNTs in O₂-saturated 0.5 M H₂SO₄. Scan rate = 5 mVs⁻¹ & T = 25°C.

The nature of support material also influences the ORR activity of the composite materials. So, to examine the influence of the catalyst support, the 32wt% Pd 8wt% Co alloy nanoparticles were also prepared on MWCNTs and investigated their ORR activity under similar experimental conditions as employed in the study of the same alloy catalyst obtained on the GNS support. LSV curves shown in Fig. 4.4.6 indicate that the ORR performance of the Pd-Co alloy is greatly improved when obtained on the GNS support rather than on
MWCNTs. Also, the onset of the reduction wave gets shifted towards the higher positive potential (Fig.4.4.6), which can be ascribed to greatly enlarged geometrical surface area and better electron transport properties of the GNS support.

To obtain kinetic information on this process, the reaction was carried out under steady – state conditions at a rotating disk electrode (RDE), Fig.4.4.7. The most active bimetallic catalyst, 32wt% Pd 8wt% Co/GNS, of the investigation was chosen for this purpose and deposited at the disk (dia. 0.3 cm) of a rotating disk electrode (RDE) and subsequently, LSV curves at the slow scan rate of 2 mV s\(^{-1}\) and varying rotations were recorded in O\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) at 298 K (Fig.4.4.7).

![Fig4.4.7. Linear scan voltammograms of 32wt % Pd 8wt% Co/GNS at varying rotations in O\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\); scan rate = 2 mVs\(^{-1}\); & T = 25ºC.](image)

Curves shown in Fig.4.4.7 do not exhibit a clear limiting current region. In the diffusion limited region, the current increased with the rotation velocity. The observation of LSV curves of the electrode at varying rotations indicates that at the higher potentials the ORR is a mixed diffusion – kinetic controlled process. Therefore, the measured disk current density (\(j\)) at a potential follows the relation (Markovic et al., 1997; Wang et al., 2003),

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}
\]

\[\text{..................................................(8)}\]

where \(j_k\) and \(j_d\) represent the currents, controlled by electron transfer kinetics and mass transport (mainly diffusion) properties, respectively.
The catalytic (kinetic) current can be determined using the Koutecky-Levich relation (Gileadi, 1993)

\[
\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B \omega^{1/2}} \quad \text{..........................}(9)
\]

Where \( \omega \) is the electrode rotation in revolutions per minute (rpm) and \( B \) is the Levich constant. The latter can be given as, (Yang et al., 2012)

\[
B = 0.2 n F C_{O_2} D_{O_2}^{2/3} \nu^{-1/6} \quad \text{..........................}(10)
\]

where 0.2 is a constant, \( C_{O_2} \) is the concentration of \( O_2 \) dissolved in the bulk electrolyte, \( n \) is the number of electrons transferred per molecule of \( O_2 \) reduced, \( F \) is the Faraday constant, \( D_{O_2} \) is the diffusion coefficient of oxygen in solution, \( \nu \) is the kinematic viscosity of sulphuric acid.

4.4.2.3 K-L Plot

The kinetic and diffusion current densities, have been calculated by constructing the linear Koutecky-Levich, L-K, (i.e. \( 1/J \) versus \( 1/\omega^{1/2} \)) plots at different constant potentials, as shown in Fig.4.4.8, and measuring the intercept (\( 1/J = 1/J_k \) for \( 1/\omega^{1/2} = 0 \)) and slope (= \( 1/B \)) of these linear curves. Values of \( j_k \) and \( B \), so obtained, are listed in Table 4.4.3. Values of slope listed in Table 4.4.3 seem to slightly decrease with the increase of the cathodic overpotential; the average value of the slope being \( 8.44 \pm 0.45 \times 10^{-2} \text{ mA}^{-1} \text{ cm}^2 \text{ rpm}^{-1/2} \) in the potential range, 0.4-0.3 V vs. RHE. The average slope, thus determined, is somewhat lower than the theoretical slope, \( 9.41 \times 10^{-2} \text{ mA}^{-1} \text{ cm}^2 \text{ rpm}^{-1/2} \) (Yang et al., 2012). The theoretical slope was computed by using Equation (7) and considering \( n = 4 \), \( F = 96485 \text{ coulomb} \), \( C_{O_2} = 1.1 \times 10^{-6} \text{ mol cm}^{-3} \), \( D_{O_2} = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \), \( \nu = 1.0 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1} \), electrolyte = 0.5 M H\(_2\)SO\(_4\).

Table 4.4.3: Estimate of kinetic values for ORR at the catalytic film of 32wt% Pd 8wt% Co/GNS on glassy carbon disk (0.3 cm dia.) in 0.5 M H\(_2\)SO\(_4\); scan rate: 2 mV s\(^{-1}\), rotation speed: 1600 rpm T = 25ºC.

<table>
<thead>
<tr>
<th>E / V</th>
<th>( j_d ) mA cm(^{-2} )</th>
<th>( \text{Slope (}=1/B)) mA(^{-1} \text{ cm}^2 \text{ rpm}^{1/2} )</th>
<th>( B ) mA cm(^{-2} \text{ rpm}^{1/2} )</th>
<th>( J_d (=B \omega^{1/2})/\text{mA cm}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>3.42</td>
<td>8.9</td>
<td>0.112</td>
<td>4.48</td>
</tr>
<tr>
<td>0.38</td>
<td>3.92</td>
<td>8.8</td>
<td>0.114</td>
<td>4.56</td>
</tr>
<tr>
<td>0.35</td>
<td>4.37</td>
<td>8.4</td>
<td>0.119</td>
<td>4.76</td>
</tr>
<tr>
<td>0.33</td>
<td>4.90</td>
<td>8.1</td>
<td>0.123</td>
<td>4.92</td>
</tr>
<tr>
<td>0.30</td>
<td>5.43</td>
<td>8.0</td>
<td>0.125</td>
<td>5.00</td>
</tr>
</tbody>
</table>
Thus, the result shows that the ORR in 0.5 M H₂SO₄ follows 3.6 ($\approx 4$) electron pathway in the potential region, 0.30 - 0.40 V vs. RHE. Zhang et al., (2004) also found similar parallel straight lines for K-L plots indicating four-electron reduction of O₂ on Pt/Pd (111) surface in 0.1 M HClO₄. Recent studies of ORR on Pd₀.₅NiₓSe₀.₅₋ₓ(Ramos-Sanchez et al., 2010), Pd deposited on porous carbon paper (Rego et al. 2012), IrCo/C (Yang et al. 2012) and Pd nanoparticles/MWCNTs (Jukk et al., 2012) in H₂SO₄ solution also exhibited a four-electron charge transfer pathway for electroreduction of O₂ to H₂O.

Fig.4.4.8: $1/j$ versus $1/\omega^{1/2}$ plots constructed from Fig.4.4.7 at constant potentials.