Section 4.5

Graphene-cobaltite-Pd hybrid materials

4.5.1 Structural characterization

Already discussed in section 4.1.

4.5.2 Electrochemical characterization

The electrocatalytic activities of the composites toward oxygen reduction reaction (ORR) were studied by linear sweep voltammetry (LSV) in O$_2$-saturated 1 M KOH at 25°C. The potential range and scan rate employed were 0.354 - 1.084 V vs. RHE and 2 mV s$^{-1}$, respectively. To obtain O$_2$-saturated and deoxygenated solutions, pure O$_2$ and Ar gas were bubbled for 45 and 30 min, respectively.

4.5.2.1 Electrocatalytic activity: LSV

In the study of ORR at the rotating disk electrode (RDE) the catalyst loading is an important parameter which has to be optimized. In fact the RDE (glassy carbon, GC) surface must be uniformly covered by the thin catalytic film. For the purpose, LSV curves at varying loadings of the catalyst at the RDE were recorded at 1600 rpm in O$_2$-saturated 1M KOH at 25°C and a suitable range of the catalyst loadings (between 0.30 and 0.90 mg cm$^{-2}$), which produces nearly a constant diffusion limited current densities, were found. The study have shown that the catalyst loadings between 0.60 and 0.90 mgcm$^{-2}$ produced reproducible LSV curves with the diffusion limited current densities close to 5 mAcm$^{-2}$. Representative LSV curves recorded at varying loadings in the case of 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS hybrid material are reproduced in (Fig.4.5.1). Therefore, the ORR study has been performed by RDE with a fixed catalyst loading of 0.6 mg cm$^{-2}$ in case of each electrocatalyst.
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Fig. 4.5.1: Linear sweep voltammograms of 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS at different catalyst loadings in O$_2$-saturated 1 M KOH; scan rate = 2 mV s$^{-1}$; rotation = 1600 rpm and T = 25˚ C.

In order to optimize the composition of the complex oxide in the composites, different amounts of MnCo$_2$O$_4$ (5, 10 and 20) have been introduced into 40wt%Pd/GNS and investigated for the ORR study and results, so obtained, are reproduced in Fig. 4.5.2. From this figure it is clear that among three different amounts of the oxide introduced, 5wt% addition seems to be beneficial for the ORR. The higher additions (10 & 20wt%) of the oxide are not beneficial from electrocatalysis stand-point.

Fig. 4.5.2: Linear sweep voltammograms of 40wt%Pd-xwt%MnCo$_2$O$_4$/GNS (x = 5, 10 and 20) in O$_2$-saturated 1 M KOH; scan rate = 2 mV s$^{-1}$; rotation = 1600 rpm and T = 25˚ C.

Fig. 4.5.3(A&B) shows a comparison of ORR activities of composite electrodes, 40wt%Pd/GNS, 5wt%MnCo$_2$O$_4$/GNS and 40wt%Pd-5wt%MCo$_2$O$_4$/GNS (M = Mn, Co & Ni)
(A) and 40wt%Pd-10wt%MCo$_2$O$_4$/GNS (M= Mn, Co & Ni) at the scan rate of 2mV s$^{-1}$ and at a fixed rotation of 1600 rpm in O$_2$-saturated 1M KOH at 25˚C.

Results shown in Fig. 4.5.3 (A and B) demonstrate that the hybrid composite with 5wt%MnCo$_2$O$_4$ has the superior ORR activity in comparison to other composites of the present study. It is noteworthy that 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS hybrid prepared by us exhibited superior ORR activity to 40wt%Pt/NC and 40wt%Pt/GNS also, particularly in the mixed kinetics diffusion-control region, as is quite apparent from LSV curves shown in Fig.4.5.4. These results indicate that the 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS hybrid catalyst could be considered as the promising electrocatalyst material for use as cathode in alkaline fuel cells. The comparison of the electrocatalytic activities of the composites based on values of the current densities observed at a constant potential, $E = 0.850$ V vs. RHE, the catalysts can be placed in the activity order: 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS ($j = 4.06$ mA cm$^{-2}$) $>$40wt%Pd-5wt%NiCo$_2$O$_4$/GNS ($j = 3.01$ mA cm$^{-2}$) $>$40wt%Pd/GNS ($j = 2.86$ mA cm$^{-2}$) $>$40wt%Pd-5wt%Co$_3$O$_4$/GNS ($j = 2.72$ mA cm$^{-2}$). However, values of the specific activity ($= I$, mA/EASA, cm$^2$) of all three hybrid catalysts including the base one (40wt%Pd/GNS) were found to be nearly the same, i.e., 0.062±0.003 mA cm$^{-2}$. Estimates of the EASA were 4.4, 3.5 and 3.2 cm$^2$ for 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS, 40wt%Pd-5wt%NiCo$_2$O$_4$/GNS and 40wt%Pd-5wt%Co$_3$O$_4$/GNS whereas 5.6, 3.6 and 3.3 cm$^2$ for 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS, 40wt%Pd-10wt%NiCo$_2$O$_4$/GNS and 40wt%Pd-10wt%Co$_3$O$_4$/GNS, respectively. The mass of the catalytic film over the disk electrode and the scan rate used in the EASA determination were 0.60 mg cm$^{-2}$ and 2mV s$^{-1}$, respectively.
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Fig. 4.5.4: Linear sweep voltammograms of 40wt%Pd-5wt%MCo$_2$O$_4$/GNS, 40wt%Pt/GNS and 40wt%Pt/NC, prepared under similar experimental condition, at 1600 rpm in O$_2$-saturated 1 M KOH; scan rate = 2 mV s$^{-1}$; catalyst loading = 0.60 (i.e., Pd = 0.24) mg cm$^{-2}$ and T = 25˚C.

The electrode kinetics study has been performed on active 40wt%Pd-5wt%MCo$_2$O$_4$/GNS (M = Mn, Co and Ni) only. For the purpose, LSV curves of hybrid electrodes containing Pd-5wt%MCo$_2$O$_4$/GNS were recorded at varying rotations in O$_2$-saturated 1 M KOH at 25˚C. Features of LSV curves obtained for all the hybrid catalysts were similar. LSV curves thus obtained for each composites i.e. 40wt%Pd-5wt%Co$_3$O$_4$/GNS, 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS and 40wt%Pd-5wt%NiCo$_2$O$_4$/GNS are given in Fig. 4.5.5 A, B & C, respectively.
Fig. 4.5.5: Linear sweep voltammograms of 40wt%Pd-5wt%Co₃O₄/GNS (A), 40wt%Pd-5wt%MnCo₂O₄/GNS (B) and 40wt%Pd-5wt%NiCo₂O₄/GNS (C) at varying rotations in O₂-saturated 1 M KOH; scan rate = 2 mV s⁻¹; catalyst loading = 0.60 (i.e., Pd = 0.24) mg cm⁻² and T = 25°C.

4.5.2.2. K-L Plot

Fig. 4.5.6 (A,B&C) shows the K-L plots for ORR on composites, 40wt%Pd-5wt%Co₃O₄/GNS, 40wt%Pd-5wt%MnCo₂O₄/GNS and 40wt%Pd-5wt%NiCo₂O₄/GNS at constant potentials. A suitable potential region wherein all LSV curves determined at varying rotations deviate significantly, were chosen to extract the kinetic data (Mayrhofer et al., 2008). According to Fig. 4.5.5, the mixed kinetic diffusion-control region, 0.950 - 0.80 vs. RHE is taken for evaluation of the kinetic information. At more negative potentials (< 0.80 V), the mass transport-limited current becomes significant where a dependence of j upon rotation rate is observed. With increasing the rotation rate, the limiting current increased due to increase in the oxygen diffusion rate from bulk to the electrode surface. Thus, the overall measured j, is mainly the sum of contributions of the kinetic current density, j_k, and the diffusion limiting current density, j_d. Both have been analyzed from the RDE data using the Koutecky-Levich (K-L) equation (8 to 10 in previous section). Theoretical value of the Levich constant, B, was estimated using relation (10) and values of Co₂ (=8.4 x 10⁻⁴ mol L⁻¹), ν (= 1.1 x 10⁻² cm² s⁻¹) and D_O₂ (=1.65 x 10⁻⁵ cm² s⁻¹) reported in the literature (Lee et al. 2011) and found to be 8.91 mA⁻¹ cm² rpm¹/².
Fig. 4.5.6: $1/j$ versus $1/\omega^{1/2}$ plots constructed from Fig. 4.5.5 for 40wt%Pd-5wt%Co$_3$O$_4$/GNS (A), 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS (B) and 40wt%Pd-5wt%NiCo$_2$O$_4$/GNS (C) at constant potentials.

From Eq. (1) the K-L plots ($j^{-1}$ vs. $\omega^{-1/2}$) were constructed and value of the intercept (at $1/\omega^{1/2} = 0$) and the slope of each K-L curve were determined. Values of the intercept and slopes, thus determined, were used to estimate values of $j_k$, $B$, $j_d$, and $n$ (Table 4.5.1). A set of seven K-L plots constructed for the electrode, 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS at different constant potentials chosen in the potential region, 0.774-0.879 V vs. RHE, are shown in Fig. 11. As $j_k$ represents the intrinsic activity and is a function of potential, its value is given at a constant potential ($E = 0.834$ V vs. RHE) for all the hybrid materials in Table 4.5.1.
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Table 4.5.1: Estimate of electrode kinetic parameters for ORR on 40wt\%Pd-5wt\%MCrO\textsubscript{4}/GNS (M = Mn, Co and Ni) in O\textsubscript{2}-saturated 1 M KOH at 25\(^\circ\)C; geometrical area of GC disk = 0.07 cm\(^2\), catalyst loading = 0.60 (i.e., Pd = 0.24) mg cm\(^{-2}\), scan rate = 2 mV s\(^{-1}\), rotation speed = 500 - 2000 rpm.

<table>
<thead>
<tr>
<th>M</th>
<th>(j_k) mA cm(^{-2}) at E = 0.834V vs.RHE</th>
<th>(1/B) (\text{mA}^{-1} \text{cm}^{-2} \text{rpm}^{-1/2})</th>
<th>(J_d) mA cm(^{-2}) at 1600 rpm</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>12.4</td>
<td>(7.9 \pm 0.9) (\text{0.879 - 0.774V})</td>
<td>~4.9~</td>
<td>~3.6~</td>
</tr>
<tr>
<td>Ni</td>
<td>7.95</td>
<td>(7.4 \pm 0.9) (\text{0.844 - 0.764V})</td>
<td>~5.5~</td>
<td>~3.3~</td>
</tr>
<tr>
<td>Co</td>
<td>5.87</td>
<td>(6.8 \pm 0.8) (\text{0.844 - 0.764V})</td>
<td>~5.9~</td>
<td>~3.1~</td>
</tr>
</tbody>
</table>

Values of slope (1/B) seem to slightly decrease with the increase of the cathodic potential; the average values of slope obtained on each catalyst are given in Table 4.5.1. The value of n is found to be 3.6, which is close to 4 in the case of the ORR study on 40wt\%Pd-5wt\%MnCo\textsubscript{2}O\textsubscript{4}/GNS, over the whole range of potentials employed. This shows that the ORR in 1 M KOH at room temperature follows essentially 4 e\(^-\) pathway in the potential region, 0.879 - 0.774 V vs. RHE. Recently, Seo et al. (2011) also reported 4e\(^-\) pathway of ORR on 60wt\%Pd/GNS and 60wt\%Pt/GNS in 0.1 N NaOH; 4e\(^-\) pathway of ORR on Pt has been reported in many studies (Adzic, 1998; Sarapuu et al., 2008; Li et al., 2009b).

The lowering of the n-value demonstrates that the ORR follows 4e\(^-\) and 2e\(^-\) paths simultaneously. However, the contribution of 2e\(^-\) path decreases when Co is replaced by Mn or Ni partially in the Co\textsubscript{3}O\textsubscript{4} spinel structure.

4.5.2.3. Tafel Plot

Fig. 4.5.7 shows the Tafel plots for composites 40wt\%Pd-5wt\%Co\textsubscript{3}O\textsubscript{4}/GNS (A), 40wt\%Pd-5wt\%MnCo\textsubscript{2}O\textsubscript{4}/GNS (B) and 40wt\%Pd-5wt\%NiCo\textsubscript{2}O\textsubscript{4}/GNS (C). To construct the Tafel plot, the kinetic current was determined using the relation, \(j_k = j \times j_d / (j_d - j)\), at varying potentials and at a constant electrode rotation, 1600 rpm. \(j_d / (j_d - j)\) is the mass-transport correction term (Rao et al., 2011). \(j_d\) value was noted from the LSV curve determined at 1600 rpm for each hybrid catalyst. The Tafel plot (E vs. log \(j_k\)) on 40wt\%Pd-5wt\%MnCo\textsubscript{2}O\textsubscript{4}/GNS shown in Fig. 4.5.7 (B) shows two linear regions, one with a slope of 45 mV at low overpotentials (E = 0.934 – 0.884 V vs. RHE) and the other one with a slope of 70 mV at higher overpotentials (E = 0.854 – 0.784 V vs. RHE). Two similar Tafel slopes on 30\%Pt/C in 1M NaOH were also observed by Ramaswamy and Mukerjee (Ramaswamy et al., 2011). Liang et al., (2011) have also recently reported a low Tafel slope of 42 mV on Co\textsubscript{3}O\textsubscript{4}/N-GNS in 0.1 M KOH. However, E vs. log \(j_k\) plots for other hybrids containing CoCo\textsubscript{2}O\textsubscript{4} Fig. 4.5.7 (A) and
NiCo$_2$O$_4$ Fig. 4.5.7 (C) prepared by us exhibited only a single slope of 68-70 mV over the potential range, ~ 0.984 -0.834 V vs. RHE. Tafel slope of 70 mV for ORR observed on 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS electrode is close to those found on platinum in acid/alkaline solutions (Sarapuu et al., 2008; Rao et al., 2011; Jiang et al, 2009b; Cochell et al., 2012).

Fig.4.5.7: E vs. log $j_k$ plot for ORR on 40wt%Pd-5wt%Co$_3$O$_4$/GNS (A), 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS (B) and 40wt%Pd-5wt%NiCo$_2$O$_4$/GNS (C) at 1600 rpm, scan rate = 2 mV s$^{-1}$ at 25$^\circ$C.

4.5.2.3. Stability Test
Fig. 4.5.8 shows the stability of the ORR active composite electrodes, 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS and 40wt%Pd-5wt% MnCo$_2$O$_4$/GNS, tested at $E = 0.654$ V vs. RHE for 6 h in 1M KOH solution at 25˚C. For comparisons, 40wt%Pt/NC and 40wt%Pt/GNS electrodes were also tested for their stabilities under identical experimental conditions (Fig. 4.5.8). Pt electrodes were prepared by employing the similar procedure as was used for the preparation of other electrodes of the investigation. Chronoamperogram ‘a’ in Fig. 4.5.8 show that in the case of 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS, after application of the constant potential, the ORR current attains its highest value within 4 min and remained practically constant throughout the experiment. Whereas, the ORR current initially observed on 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS (Fig. 4.5.8.b) and Pt electrodes (Fig. 4.5.8 c and d) undergo a gradual decay with passage of time, the magnitude of decrease in current being less on the 40wt%Pt/GNS electrode compare to that on 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS. Recently, Liang et al. has also observed a gradual decay in the ORR current density on Pt/C catalyst with passage of time because of surface oxide and particles dissolution in alkaline solutions (Liang et al., 2012). Thus, results substantiate that the ORR activity performance of the 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS hybrid electrode is superior to 40wt%Pt/NC or 40wt%Pt/GNS electrode. Similar stability has not been found, to our knowledge, for other Pt- or Pd-based catalysts under alkaline conditions.

Fig. 4.5.8: Chronoamperograms of 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS, 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS, 40wt%Pt/GNS and 40wt%Pt/NC at $E = 0.654$ V in O$_2$-saturated 1 M KOH at 1600 rpm (25˚C).