ABSTRACT

The present thesis is comprised of studies on “Preparation and characterization of nanosstructural composite materials for direct alcohol fuel cell applications”. Novel graphene supported Pd based composite materials have been prepared and characterized for the methanol electrooxidation and oxygen reduction reactions in alkaline/acidic medium.

Composite materials synthesized under the title investigation are:

(i) Bimetallic Pd and Co dispersed on GNS

(ii) 40wt%Pd-xwt%MCo₂O₄/GNS (M=Mn, Co or Ni and x=5 and 10)

(iii) 40wt%Pd-xwt%Mn₂O₄/GNS (M=Mn, Co, Fe or Cu and x=5 and 8)

(iv) 40wt%Pd-xwt%MnMoO₄/GNS (x=2.5, 8, 10, 20 and 30)

Graphene supported Pd based catalysts have been prepared by microwave-assisted polyol reduction method. Spinel oxides, cobaltites (Co₃O₄, MnCo₂O₄ and NiCo₂O₄) and manganites (Mn₃O₄, CoMn₂O₄, FeMn₂O₄ and CuMn₂O₄) used as precursors in preparation of hybrids. These oxides were prepared by a precipitation method (Srirapu et al., 2013; Singh et al., 2000a; Lal et al., 2001). Graphene was synthesized by modified Hummers and Offenmans method (Hummers et al., 1958). MnMoO₄ was prepared using a method similar to that reported in (Kumar et al., 2011).

 Powders of the catalysts were transformed in the form of film on the glassy carbon (GC) support by an ink-painting method. For the ink preparation, the calculated amount of the catalyst powder was mixed with ethanol-water mixture (2:1). The ink was casted onto the pre-treated GC plate, left for air dry and 1% Nafion solution was then placed at the catalyst surface. An electrical contact with catalyst film was made by using thin copper wire, silver paste and Araldite epoxy. Only ~ 0.5 cm² geometrical area of the catalytic film on GC was used in the investigation and the remaining surface was covered with Araldite epoxy. While in the case of RDE study the geometrical area of the electrode was, 0.07 cm².

 The hybrid catalysts, mentioned above, were characterized structurally by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Transmission electron microscopy (TEM). The electrochemical characterizations of materials were made by Cyclic voltammetry (CV), CO-stripping voltammetry, Linear sweep voltammetry (LSV) and chronoamperometry.
Pd-Co/GNS catalyst electrodes being inactive toward methanol oxidation have been investigated as methanol tolerant cathode materials for ORR in 0.5 M H$_2$SO$_4$ at 25°C. However, hybrids 40wt%Pd-xwt%MCo$_2$O$_4$/GNS and 40wt%Pd-xwt%Mn$_2$O$_4$/GNS were investigated as bifunctional electrocatalysts for both MOR and ORR in 1M KOH at 25°C. The 40wt%Pd-xwt%MnMoO$_4$/GNS hybrid catalysts are found to be catalytically active toward MOR and quite less active toward ORR in 1M KOH at 25°C, their catalytic activities were examined for MOR only.

Details of the results, obtained, are summarized in following lines:

The XRD study have shown that in all the Pd-based hybrid catalysts, Pd follows the face centered cubic (fcc) crystalline structure with characteristic diffraction peaks at $2\theta = \sim 40^\circ, \sim 46.5^\circ$ and $\sim 68.2^\circ$, which correspond to (111), (200) and (220) planes, respectively. It is noteworthy that none of the oxide components (MCo$_2$O$_4$, MMn$_2$O$_4$ or MnMoO$_4$) in the hybrid materials indicated its presence in X-ray diffractograms. Estimates of the crystallite size for Pd in different composites ranged between 3 and 11 nm.

TEM analyses for all the composites show the good dispersion of catalyst nanoparticles (NPs) on the graphene nano sheets (GNS). The Pd NPs look to be spherical in shape and exist in cluster form on the GNS surface, whereas the oxide (MnCo$_2$O$_4$) particles look like nano dots (< 5 nm) and produce very uniform distribution on the GNS surface. The dispersion of Pd NPs seems to be improved with limited addition of the oxide (cobaltite, manganite or molybdate) or Co metal. The best dispersion of Pd is observed with MnCo$_2$O$_4$. At high resolution, some lattice fringes are observed which indicate that the NPs are crystalline in nature. Co substitution into Pd/GNS composite causes reduction in particle size (up to 4.3 nm) whereas oxide addition somewhat increases the size (up to 11 nm). Values of the particle size shown by TEM analyses are nearly in the same range as obtained by XRD. This result also demonstrates good dispersion of the NPs on the GNS support.

The XPS study of Pd/GNS shows two characteristic photo peaks, Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ at B.E=335.6 and 340.7 eV respectively, for the metallic Pd. The comparison of binding energies of Pd observed for Pd/GNS and Pd-oxide/GNS samples shows a negative shift in binding energy (less than 0.3 to 1.1 eV), which indicates that the Pd NPs might interact with the oxide and that there seems the transfer of electron from oxide to Pd.
Abstract

Co 2p spectrum of composite shows that on pure oxide surface Co present in Co$^{3+}$/Co$^{4+}$ states, while that in Co$^{2+}$/Co$^{3+}$ states on the composite surface.

Similarly, Mn 2p spectra show that in the case of pure cobaltites as well as pure manganites, Mn is present in Mn$^{2+}$/Mn$^{3+}$ states while it is present in Mn$^{3+}$/Mn$^{4+}$ or Mn$^{2+}$/Mn$^{3+}$ states with dominance of the higher oxidation state on the composite surface.

Ni 2p spectra show that Ni is present in Ni$^{2+}$/Ni$^{3+}$ states in case of both pure oxides as well as composites with dominance of Ni$^{3+}$ in the case of composites.

Fe 2p spectra show its presence mainly in Fe$^{3+}$ state on the surface of the composite and Cu 2p spectra show that Cu is present in Cu$^{2+}$ state at the surface of composites whereas it is present in Cu$^{0}$/Cu$^{1+}$ states on the pure oxide.

Cyclic voltammetry (CV) of composite electrodes recorded at the scan rate of 50 mV s$^{-1}$ in the potential region from 0.110 to 1.210 V vs. RHE in 1 M KOH, and from -0.058 to +1.542 V vs. RHE in 0.5 M H$_2$SO$_4$ without containing 1 M CH$_3$OH at 25 °C. Each curve exhibited well defined cathodic and corresponding anodic peaks for the adsorption and desorption of hydrogen atom in the potential region from 0.40 to 0.54 V vs. RHE and a strong cathodic peak at about 0.60 to 0.70 V vs. RHE for the reduction of palladium (II) oxide. The latter has been formed as a result of oxidation of Pd under anodic condition. In 0.5 M H$_2$SO$_4$, 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. The wave-like shape of voltammograms on the positive-going scan and prior to the commencement of O$_2$ evolution reaction can be ascribed to a slow electrochemical oxidation of the palladium surface into palladium (II) oxide. A relatively strong cathodic peak observed at 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.

The electrochemically active surface area (EASA) of the composite electrodes have been estimated by determining the coulombic charge, Q, for the complete reduction of palladium (II) oxide into Pd (0). Results have shown that the EASA of Pd/GNS (~ 30 cm$^2$) increases with introduction of manganite (or molybdate) from 2 to 8 wt% and of cobaltite from 2 to 10 wt%, the magnitude of increase being the greatest with Pd-10wt%MnCo$_2$O$_4$/GNS (~50 cm$^2$). The increase in EASA can be attributed to increase in dispersion of Pd NPs in the presence of oxides. A higher addition of the oxide (5 wt%) decreased the EASA, which may be due to agglomerate formation.

CV curves of all the electrocatalysts recorded in the potential range from 0.110 to 1.210 V vs. RHE or 0.37 to 1.17 V vs. RHE in 1 M KOH + 1 M CH$_3$OH exhibited two
characteristic anodic (oxidation) current peaks, one in the forward scan (i.e. under anodic condition) and the other one in the reverse scan (i.e. under cathodic condition). The results show that the 40wt%Pd-8wt%CoMn$_2$O$_4$/GNS catalyst exhibits the greatest apparent as well as the specific activity (SA = 1 (mA)/ EASA (cm$^2$)) towards MOR in 1M KOH. The catalytic activity of Pd/GNS increases 2 times with 8% oxide (10% for cobaltite) addition. A higher or a lower addition of oxide had adverse effect.

The CV of Pd-Co/GNS electrodes, in 0.5M H$_2$SO$_4$ + 1M CH$_3$OH, did not indicate any oxidation-reduction peak for methanol, suggesting that they are tolerant to methanol oxidation reaction. The activities of different catalysts of the present investigation towards MOR at a constant potential (E = 0.610 V vs. RHE) in 1M KOH + 1M CH$_3$OH are shown by a bar diagram in Fig. 1.

The CO stripping voltammetry of the Pd-oxide(cobaltite)/GNS composites recorded in the potential range from 0.110 to 1.210 V vs. RHE in 1 M KOH at a scan rate of 50 mVs$^{-1}$ have shown two well separated CO oxidation current peaks under anodic conditions. However, stripping voltammetry of MnCo$_2$O$_4$/GNS did not indicate any oxidation peak. These results indicate that there could be, at least, two different kinds of Pd active sites, even on pure Pd surface, where CO adsorption can take place. It appears that CO gets adsorbed strongly on one kind of Pd sites while less strongly, on the other kind. On the other hand the CO stripping voltammetry of the hybrid catalysts containing MnMoO$_4$ under similar condition indicated one strongly and other one very weak (feable) CO oxidation peak under anodic conditions. The anti CO poisoning abilities of Pd-cobaltite/GNS catalysts followed the order: 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS > 40wt%Pd-10wt%NiCo$_2$O$_4$/GNS > 40wt%Pd-10wt%Co$_3$O$_4$/GNS > 40wt%Pd/GNS. Whereas in the case of Pd-MnMoO$_4$/GNS composites the anti-poisoning abilities of hybrid catalysts showed the order: 40wt%Pd-8wt%MnMoO$_4$/GNS > 40wt%Pd-10wt%MnMoO$_4$/GNS > 40wt%Pd-5wt%MnMoO$_4$/GNS > 40wt%Pd-2wt%MnMoO$_4$/GNS > 40wt%Pd-20wt%MnMoO$_4$/GNS >40wt%Pd/GNS.

The chronoamperometry of the composite electrodes have been carried out at 0.610 V (or 0.626 V) vs. RHE in 1 M KOH + 1 M CH$_3$OH at 25°C. All the oxide added Pd/GNS composites shows fairly stable performance during their 2hr test. Estimates of the increase in activities (%) of hybrid electrodes in relation to the base electrode were ~170%, ~120% and ~185% in case of 40wt%Pd-8wt%MnMoO$_4$/GNS, 40wt%Pd-8wt%CoMn$_2$O$_4$/GNS and 40wt%Pd-10wt%MnCo$_2$O$_4$/GNS, respectively. Thus, the addition of a controlled amount of oxide into Pd/GNS matrix enhances the poisoning tolerance of the base electrode greatly.
Fig.1. The comparative electrocatalytic activities for MOR at 0.610 V vs. RHE in 1 MKOH + 1 MCH$_3$OH at 50 mVs$^{-1}$ for all the Pd-based electrocatalysts investigated in the present study.

Hybrids of Pd and GNS with an oxide of cobaltite and manganite spinel families having general formula 40wt%Pd-5wt%MCo$_2$O$_4$ (M= Mn, Co or Ni)/GNS and 40wt%Pd-5wt%MMn$_2$O$_4$ (M= Mn, Co, Fe or Cu)/GNS, have also been investigated for the ORR in O$_2$-saturated 1M KOH by rotating disk electrode technique. Results have shown that among hybrid catalysts investigated, 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS exhibits the greatest ORR activity. The ORR activity of this electrode is also found to be superior to Pt/GNS. For a better understanding, the comparative ORR activities of various electrodes investigated in the present dissertation have been displayed at E=0.850 V vs RHE and at 1600 rpm through a bar diagram as shown in Fig.2. The RDE study on 40wt%Pd-5wt%MCo$_2$O$_4$ (M=Mn, Co, Ni)/GNS has shown that ORR occurs by ~3.4±0.2 (i.e. 4) electron (n) path way (The ORR study on 40wt%Pd-5wt%MMn$_2$O$_4$/GNS (M=Mn, Co, Fe, Cu)/GNS also indicated an average of ~4 electron transfer process). However n-values (~4) estimated at lower overpotentials somewhat decreased at the high cathodic overpotentials. This indicates that the ORR proceeds through both the direct 4e$^-$ and the 2e$^-$ (i.e. peroxide) mechanistic paths at higher overpotentials. The Tafel slope (1/B) for ORR on 40wt%Pd-5wt%MnCo$_2$O$_4$/GNS showed two distinct regions, one with a slope of 45 mV at low and the other one with a slope of 70 mV at higher overpotentials. Whereas hybrids with other cobaltites exhibited a single slope of ~70 mV. Among hybrid catalysts with manganites 40wt%Pd-5wt%CoMn$_2$O$_4$/GNS showed a slope of 43 mV while the other had higher value of slope.
Fig.2. The comparative ORR activities at 0.850 V vs. RHE in 1 MKOH at 1600 rpm, at 2mVs\(^{-1}\) for all the hybrid catalyst investigated in the present study. The bifunctional Pd-oxide-GNS electrodes particularly 40wt\%Pd-10wt\%MnCo\(_2\)O\(_4\)/GNS and 40wt\%Pd-8wt\%CoMn\(_2\)O\(_4\)/GNS exhibited excellent stabilities under both methanol oxidation as well as oxygen reduction conditions in 1M KOH. The active 40wt\%Pd-8wt\%MnMoO\(_4\)/GNS also demonstrated higher stability compared to 40wt\%Pd/GNS.

The ORR study on Pd-Co/GNS composites, shows that Co substitution from 3.64 to 8 wt\% increases ORR activity while further addition reduces the activity, as is quite apparent from the bar diagram shown in Fig.3. RDE analysis demonstrated that the ORR follows 3.6 (~4) electron pathway. All the bimetallic Pd-Co/GNS composites show good methanol tolerance. Also graphene supported Pd-Co shows better ORR performance than the corresponding multiwalled carbon nano tubes (MWCNTs).

Fig.3. The comparative ORR activities of Pd-Co/GNS at 0.442 V vs. RHE under stationary condition in 0.5M H\(_2\)SO\(_4\) at 2mVs\(^{-1}\).
The important finding of the work described above can be represented in brief as follows:

1. The oxide introduced into the Pd/GNS matrix interacts strongly with both graphene as well as palladium resulting in modification of electronic properties of the hybrid material greatly.

2. The nano-composites, 40wt%Pd-10wt%MCo₂O₄/GNS (M=Co, Mn & Ni), efficiently oxidize methanol and reduce oxygen in alkaline medium.

3. Among 40wt%Pd-10wt%MCo₂O₄/GNS (M = Co, Mn or Ni) nanocomposite catalysts, the 40wt%Pd-10wt%MnCo₂O₄/GNS shows the greatest catalytic activity for both the fuel cell reactions, methanol oxidation as well as oxygen reduction in 1M KOH.

4. The 40wt%Pd-xwt%MnMoO₄/GNS nanocomposites are quite active for methanol oxidation, the activity being the greatest with x=8. However, the presence of MnMoO₄ in the Pd/GNS is detrimental for the oxygen reduction reaction.

5. The catalytic activity of 40wt%Pd-8wt%MnMoO₄/GNS was almost double, to that of base electrode (40wt%Pd/GNS).

6. The nanocomposites, (40-x)wt%Pd-xwt%Co/GNS (3.64 ≤ x ≤ 13.33) do not oxidize methanol in 0.5 M H₂SO₄ but they efficiently reduce oxygen. Of these, 32wt%Pd-8wt%Co/GNS shows the greatest ORR activity.

7. Among all Pd-oxide/GNS composites studied, 40wt%Pd-8wt%CoMn₂O₄/GNS demonstrates the greatest catalytic activity towards MOR. Active composite electrodes of each series follow the MOR activity order: 40wt%Pd-8wt%CoMn₂O₄/GNS>40wt%Pd-8wt%MnMoO₄/GNS>40wt%Pd-10wt%MnCo₂O₄/GNS.

8. Among all composite electrodes studied for the ORR, 40wt%Pd-5wt%MnCo₂O₄/GNS demonstrates the highest catalytic activity. Its activity is even superior to Pt/GNS electrode. The ORR activity of the 40wt%Pd-5wt%CoMn₂O₄/GNS is slight inferior to 40wt%Pd-5wt%MnCo₂O₄/GNS.

9. The nanocomposite, 40wt%Pd-8wt%Mn₂O₄/GNS (M=Mn, Fe, Co, Cu)/GNS also efficiently oxidize methanol and reduce oxygen in alkaline solution, the observe catalytic influence, however, being the greatest with 40wt%Pd-8wt%CoMn₂O₄/GNS for both fuel cell reactions.

10. The active composite electrodes containing the oxide are greatly CO poisoning tolerance and highly stable. Similar stability has not been shown by other Pd- or Pt-based fuel cell catalysts reported in the literature.