CHAPTER 6

HYBRID OF MESOPOROUS SPINEL COBALT-MANGANESE OXIDE AND GRAPHENE AS ELECTROCATALYSTS FOR OXYGEN REDUCTION REACTION

6.1 INTRODUCTION

The energy demand in the present time stimulated the development of alternative energy conversion and storage devices such as fuel cell and batteries in its edge. In particular, electrochemical conversion of $\text{O}_2$ to $\text{H}_2\text{O}$ in aqueous media (ORR) and its reverse reaction, $\text{H}_2\text{O}$ to $\text{O}_2$ (water oxidation or oxygen evolution OER), attract widespread attention because these ubiquitous reactions can realize ultra high efficient energy conversion without heat loss. The ORR is the common cathode reaction for different low temperature fuel cells (Kinoshita 2002). A great deal of progress has been made in the design of PGM for oxygen reduction in both acidic and alkaline environment. Though PGMs are indubitably the best, the profuse use is limited due its high cost, low tolerance to methanol and relatively less in availability. One of the main factors which impede the commercialization of low temperature fuel cell is the use of Pt based metals as electro catalysts (Debe 2012). Therefore intensive efforts have been taken towards the development of active and durable low cost substitutes with ORR activity comparable to that of Pt/C (Zhongwei et al 2011; Jeon et al 2013). It would be extremely challenging to
design, more economically viable, abundant, nonprecious metal electro catalyst for ORR.

A series of perovskites have been investigated as active catalyst for ORR in alkaline medium. Though quite reasonable performance for decomposition of peroxide has been observed with perovskites, its degradation under cathodic operation is rather high (Carbonino et al 1998; Jorissen 2006). Besides perovskites, metal oxides having spinel structure also has been reported for its ORR activity. The main criteria for choosing an appropriate electro catalyst involves, electro catalytic activity, corrosion resistance and fabrication cost. Spinel oxides containing Ni, Cu, Co, and/or Mn have been widely reported to be active ORR catalysts in an alkaline solution. Among them, Co- and/or Mn-based spinels are most interesting due to the prominent advantages of cobalt and manganese in terms of low cost, high abundance, and multiple valences (Shoemaker et al 2009; Hamdani et al 2010). Cobalt oxides and manganese oxides show reasonable catalytic activity towards ORR in terms of their thermodynamical stability and low impedance in alkaline medium (Hamdani et al 2010). Though the individual spinel oxides such as Co$_3$O$_4$ and Mn$_3$O$_4$ are good in their intrinsic ORR activity, partial substitution of Co and Mn by other metals such as Ni, Cu, Al, Co or Mn (NiCo$_2$O$_4$, CuCo$_2$O$_4$, CuMn$_2$O$_4$, NiMn$_2$O$_4$ and AlMn$_2$O$_4$) have been proven to improve the ORR activity in alkaline solutions due to its variable cationic distribution in both tetrahedral and octahedral sites (Restovic et al 2002; Chen et al 2014).

Co substituted manganese oxides have been reported for its improved ORR and OER activities (Prabu et al 2014; Cheng et al 2011). Particle size and surface area of these oxides play a crucial role in the electro catalytic activity since the reaction occurs at the three phase boundary of
oxygen, catalyst and electrolyte; this requires active interface areas. Traditional ceramic synthetic routes for spinel oxides give large particle size with low surface area (Armijo 1969; Stein et al 1993). Spinel metal oxides with small particle size, large surface area, structure and porosity are sensitive to the preparation condition and calcination temperatures used.

Synergistic coupling of these spinel metal oxides with additives such as carbon based compounds or graphene could further improve the electrical conductivity of the semiconducting materials with more number of reactive sites (Feng et al 2012; Yang et al 2011). In this present study, we report a facile hydrothermal method to synthesize a mesoporous hybrid CoMn$_2$O$_4$/G nanostructure for the ORR in alkaline environment. The emphasis of this work laid on the rational surface structure design of CoMn$_2$O$_4$ with improved conductivity through the addition of carbonaceous graphene with large surface area. We found that the hybrid nanostructure exhibited more positive onset potential for ORR with a complete four electron transfer. The lower electrochemical impedance compared with Pt/C entails the improved interface charge transfer accompanied by methanol tolerance and long term stability which makes CoMn$_2$O$_4$/G a promising choice of alternatives for Pt/C.

6.2 EXPERIMENTAL

6.2.1 Synthesis of CoMn$_2$O$_4$/G

CoMn$_2$O$_4$/G spinel hybrid nanostructures were synthesized by a simple hydrothermal method followed by thermal annealing. In a typical procedure, 1:3 molar ratio of cobalt II chloride (CoCl$_2$, 97%, sigma Aldrich) and potassium permanganate (KMnO$_4$, ACS reagent, ≥99.0%, Sigma Aldrich) were added into an autoclave which contains 20ml of ethylene glycol
anhydrous, 99.8% , Sigma Aldrich). 100 mg of graphene powder was added to the above mixture and stirred for around 30 minutes. After heating in an electric oven at 180°C for a period of 12 h, the autoclave was cooled down to room temperature. The precipitate was separated by centrifugation and washed several times using Milli-Q water and ethanol. Finally the product was dried under vacuum at room temperature and annealed in air at 300°C for 2 h. For comparison, Co₃O₄/G, Mn₃O₄/G, and CoMn₂O₄ without graphene were also synthesized in the same way.

6.2.2 Electrode Preparation

An aliquot of 5 mg of the catalyst was suspended in a mixture of 875 µL of milli-Q® water, 220 µL of isopropyl alcohol and 20 µL of a 5 % w/w lower aliphatic alcohols - water solution of Nafion® (EW: 1100, Aldrich). 28 µL of the sample drop casted on the glassy carbon electrode and dried at 60°C in air. The final weight of the catalyst was 0.125 mg. All the electro chemical experiments have been carried out in 0.1M KOH aqueous solution.

6.3 RESULTS AND DISCUSSION

6.3.1 pXRD Analysis

Figure 6.1 depicts the crystallographic structures of synthesized CoMn₂O₄/G sample after 300°C thermal annealing. The peak around 25° attributes to the presence of graphene. Crystalline peaks corresponds to spinel structure of CoMn₂O₄ with a tetragonal crystal system appeared at 39.75° with a space group I41/amd (JCPDS No. 77-0471) (Jung et al 2014), indicating the formation of CoMn₂O₄/G hybrid nanostructure.
Figure 6.1 pXRD profiles of CoMn$_2$O$_4$/G annealed at 300°C for 2h in air

6.3.2 SEM Analysis

Figure 6.2 shows the morphology of the pure graphene flakes used in this study. After forming a hybrid with CoMn$_2$O$_4$, it appears as a flower-like morphology with nanometer sized CoMn$_2$O$_4$ (Figure 6.3).

Figure 6.2 (A) Low and (B) high magnification SEM images of graphene flakes
6.3.3 TEM Analysis

TEM image in Figure 6.4 clearly shows the small CoMn$_2$O$_4$ particles having a narrow size distribution around 5-8nm, strongly coupled with graphene flakes. No graphene-free nanoparticles or agglomerated CoMn$_2$O$_4$ were observed during the TEM examination. Controlled thermal annealing helped the nanoparticle to separately fix on the surface of the graphene flakes by retaining its nano structure forming CoMn$_2$O$_4$/G, a hybrid nanostructure.
6.3.4 BET Surface Area Measurements

N$_2$ adsorption-desorption isotherms of CoMn$_2$O$_4$/G is shown in Figure 6. 5. Using the Brunauer–Emmett–Teller (BET) method, the surface area calculated was 375 m$^2$.g$^{-1}$. The average pore size distributions were evaluated with the BJH method and the pore width lies between 5-15 nm. This mesoporous nanostructure resulted in a large BET surface area for this hybrid material.
Figure 6.5  N\textsubscript{2} adsorption-desorption isotherms and pore size distribution curve of CoMn\textsubscript{2}O\textsubscript{4}/G

6.3.5 Thermogravimetric Analysis (TGA)

The mass fraction of graphene in CoMn\textsubscript{2}O\textsubscript{4}/G hybrid was determined from TGA analysis shown in Figure 6.6. The gravimetric curves show weight loss around 80-150\textdegree C, which corresponds to the volatilization of the absorbed water. The second weight loss in the range of 350-600\textdegree C corresponds to the decomposition of graphene under air. The graphene content is estimated to be 38\% from the TGA analysis.

Figure 6.6 TGA analysis of CoMn\textsubscript{2}O\textsubscript{4}/G under air flow with a temperature ramp of 10\textdegree C min\textsuperscript{-1}
### 6.3.6 HAXPES Studies

HAXPES analysis was employed to analyze elementary composition and oxidation states of metal atoms in the CoMn$_2$O$_4$/G hybrid. Figure 6.7 shows the survey spectrum, where the different photoelectron peaks corresponding to Co 2p, Mn 2p, O 1s and C 1s, indicate that carbon, oxygen, cobalt and manganese exist in the hybrid nanostructure without any other impurities.

![Survey spectrum of CoMn$_2$O$_4$/G](image)

**Figure 6.7 Survey spectrum of CoMn$_2$O$_4$/G**

The HAXPES spectrum for Co 2p shown in Figure 6.8A exhibits two sharp peaks at 780.1±0.2 and 795.5±0.2 eV, belonging to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, and two shoulder peaks with binding energies (BE’s) at 786.1±0.2 and 802.7±0.2 eV. The peaks and their prominent shake-up satellites are typical for divalent high spin cobalt (Zhang et al 2006; McIntyre et al 1990). The shake-up process in the valence electron causes the satellite peaks above the main Co peak confirms the divalent nature of Co. It has also been confirmed from the peak separation value (Co 2p$_{1/2}$ -2p$_{3/2}$) close to 16.0 eV (Frost et al 1972). In the Mn 2p spectrum (Figure 6.8B), the Mn2p$_{3/2}$ and Mn2p$_{1/2}$ peaks at BE’s of 641.7±0.2 eV and 653.3±0.2 eV indicate that the Mn exist in trivalent form agrees with the literature values (Carver &
Schweitzer 1972). In the O1s spectrum, the peak at 529.9±0.2 eV assigned to oxide ions, whereas one small peak appeared around 531.4 ±0.2 eV is due to the hydroxide and/or absorbed water (Tan et al 1991). The BE’s recorded for Co 2p, Mn2p and O1s confirms the structure exist as Co$^{2+}$Mn$^{3+}$O$_4$. The photo emission peak corresponds to C at 284.6 ±0.2 eV suggest C=C in graphene.

![Figure 6.8 HAXPES spectra of (A) Co region (B) Mn region (C) O region and (D) C region](image)

6.5 ELECTROCHEMICAL MEASUREMENTS

6.5.1 Oxygen Reduction Reaction Activity

The ORR activity of CoMn$_2$O$_4$/G hybrid nano structure by RDE technique is presented in Figure 6.9. It shows the comparison of disk currents recorded at 2400 rpm for CoMn$_2$O$_4$/G, graphene, CoMn$_2$O$_4$+G (physical mixture), Co$_x$O$_y$/G, Mn$_x$O$_y$/G and CoMn$_2$O$_4$ respectively. ORR polarization curves were recorded in both Ar and O$_2$ saturated electrolyte and the curves are plotted after subtracting the background. At 2400 rpm, CoMn$_2$O$_4$/G hybrid nanostructure showed a remarkable ORR onset potential of around -0.028V vs Ag/AgCl reference electrode, which is higher than CoMn$_2$O$_4$+G (-0.060V)
and CoMn$_2$O$_4$ without graphene (-0.206V). The limiting current density of CoMn$_2$O$_4$/G was 9.11 mA.cm$^{-2}$. Though Co$_x$O$_y$/G showed limiting current of 9 mA.cm$^{-2}$ which is close to CoMn$_2$O$_4$/G, its onset potential (-0.089V) was less compared to CoMn$_2$O$_4$/G. The onset potential and limiting current density of Mn$_x$O$_y$ was same as that of CoMn$_2$O$_4$ +G. Both graphene and CoMn$_2$O$_4$ show poor ORR activities. In terms of half wave potential for the ORR, CoMn$_2$O$_4$/G hybrid having more positive shift compared to other metal oxides and close to that of Pt/C catalyst. The catalytic studies on Co$_x$O$_y$/G and Mn$_x$O$_y$/G could elucidate the advantages of substituted spinel oxides over single spinel oxides. The significant betterment in onset potential, half wave potential and cathodic limiting current for ORR may be attributed to the strong interaction between nanostructured CoMn$_2$O$_4$ with high surface area graphene. The reaction kinetics of this hybrid nanostructure during the ORR process has been studied by operating the RDE electrode in various rotation speeds (Figures 6.9-6.11). It is known that the limiting current increases with increase in rotation speed due to the increase in mass transport rate.

![Figure 6.9 ORR polarization curves of CoMn$_2$O$_4$, Graphene, CoMn$_2$O$_4$+G, CoO$_x$O$_y$/G, Mn$_x$O$_y$/G, CoMn$_2$O$_4$/G and Pt/C at a rotation speed of 2400 rpm in O$_2$ saturated 0.1M KOH](image)
Figure 6.10 ORR polarization curves of (A) CoMn$_2$O$_4$/G, (B) CoMn$_2$O$_4$+G and (C) CoMn$_2$O$_4$ at various rotations ranging from 400-2400 rpm at regular intervals.

Figure 6.11 ORR polarization curves of (A) Co$_x$O$_y$/G, (B) Mn$_x$O$_y$/G and (C) Graphene at various rotations ranging from 400-2400 rpm at regular intervals.
The Koutucky-Levich (K-L) plot has been displayed as inverse current (1/I) vs. inverse square root of rotation speed (ω^{-1/2}) of all the synthesized compounds shown in Figure 6.12 and 6.13. Number of electrons involved in the ORR (n) of CoMn$_2$O$_4$/G hybrid nanostructure can be estimated from the slope of K-L plot, on the basis of the Koutoucky-Levich equation derived mathematically. The number of electrons in CoMn$_2$O$_4$/G hybrid catalyst was found to be 4.01 from the potential range of -0.75 to -0.9V, proposing that ORR is driven by four-electron (4e-) pathway. Whereas the number of electrons is 1.9 in case of graphene suggesting that the ORR is dominated by two-electron process, suggesting the partial oxidation of O$_2$ followed by the formation of undesirable H$_2$O$_2$.

![Figure 6.12 Koutockey-Levich plots obtained for (A) CoMn$_2$O$_4$/G, (B) CoMn$_2$O$_4$+G and (C) CoMn$_2$O$_4$]
In addition, the number of electrons transferred has been calculated for control samples such as CoMn$_2$O$_4$, CoMn$_2$O$_4$+G, Co$_x$O$_y$/G and Mn$_x$O$_y$/G and it was 3.4, 3.2, 3.4 and 3.6 respectively. By concerning activity and electron transfer mechanism for ORR, CoMn$_2$O$_4$/G hybrid compound was better compared to other metal oxides reported here. Electrocatalytic performance of CoMn$_2$O$_4$/G is comparable with that of Pt/C in terms of onset potential and limiting current density due to its synergistic effect of the hybrid nano structure including its high surface area, mesoporous nature and strong interaction effect with graphene.

6.5.2 Chronoamperometry Analysis

It is important to have notable selectivity and durability towards ORR for the hybrid electro catalyst. The CoMn$_2$O$_4$/G hybrid structure and
commercial Pt/C catalyst were further compared by testing the methanol crossover via chronoamperometric responses at the potential of −0.5 V in O\textsubscript{2}-saturated 0.1 M KOH electrolyte, as shown in Figure 6.15. There was a drastic drop in the amperometric current of Pt/C electrocatalyst due to the methanol oxidation occurred on the surface of Pt/C, whereas no noticeable change in the current has been observed for CoMn\textsubscript{2}O\textsubscript{4}/G hybrid catalyst indicating that, it has higher selectivity towards methanol. It also displayed excellent durability with an insignificant 5% drop in relative current (I/I\textsubscript{0}) after 10000s, while Pt/C had a drop of 15%, suggesting, CoMn\textsubscript{2}O\textsubscript{4}/G hybrid not only has a higher selectivity towards ORR reaction, but also has good stability which is much important for practical applications. Therefore, the CoMn\textsubscript{2}O\textsubscript{4}/G hybrid nanostructure developed in this work could be quite promising electrocatalyst for ORR in fuel cells.

Figure 6.14  Chronoamperometric response for the CoMn\textsubscript{2}O\textsubscript{4}/G hybrid structure and commercial 20 wt% Pt/C obtained at −0.5 V in 0.1 M O\textsubscript{2} -saturated KOH solution with addition of 2 wt% methanol at the time of 2000 s
6.6 EIS ANALYSIS

An insight into the strong interface contact between $\text{CoMn}_2\text{O}_4$ and graphene has been made by Impedance spectroscopy measured at -0.1V vs Ag/AgCl, shown in Figure 6.15. A semicircle, which comprise high and low frequency region specify the two main causes which impede the constant current flow through a system. In a Nyquist plot, the high frequency region represents the electrolyte resistance and low frequency region represents the charge or mass transfer resistance. The semicircle in Figure 6.15 exhibit lower charge transfer resistances for $\text{CoMn}_2\text{O}_4$/G hybrid nanostructure compared to $\text{CoMn}_2\text{O}_4$ +G and Pt/C. It is validating our assumption of having a strong interaction between $\text{CoMn}_2\text{O}_4$ and graphene, which could improve the interfacial charge transfer between $\text{CoMn}_2\text{O}_4$ and graphene. The $\text{CoMn}_2\text{O}_4$/G hybrid shows 0.38 Kohms resistance whereas Pt/C has a charge transfer resistance of 0.5 Kohms indicating that reaction kinetics in $\text{CoMn}_2\text{O}_4$/G might be better due to the less charge transfer resistance in the interface between graphene and the spinel oxide.

![Figure 6.15](image)

**Figure 6.15** Electrochemical Impedance Spectroscopy analysis of $\text{CoMn}_2\text{O}_4$/G, $\text{CoMn}_2\text{O}_4$+G and Pt/C in $\text{O}_2$- saturated 0.1M KOH at -0.1 V (Vs Ag/AgCl) with a catalysis loading of 50 mg.cm$^{-2}$ at a rotation speed of 2025 rpm
6.7 CONCLUSIONS

CoMn$_2$O$_4$/G has been synthesized by a simple hydrothermal process followed by thermal annealing in air. The synthesized hybrid nanostructure exhibited remarkable electrocatalytic activity towards ORR due to the combined effect of structure and strong interaction of spinel oxide with graphene. The electron transfer number for CoMn$_2$O$_4$/G is 4.01 indicating that the oxygen reduction is processing via four-electron pathway. Furthermore, the CoMn$_2$O$_4$/G show higher selectivity towards methanol and better durability compared to Pt/C electrocatalyst. The better quality CoMn$_2$O$_4$/G hybrid nanostructure is a promising low-cost and effective noble metal free catalyst towards ORR. The present work gives a feasible route for the design and synthesis of hybrid materials which can be further extended to produce such materials for various energy related applications.