

Development of Two-Dimensional Material and Transition Metal Oxide based nanocomposites for Direct Methanol Fuel Cell Anode Catalyst and Supercapacitor Electrode

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Chapter 7: Conclusions and Future prospects

This chapter summarizes the primary conclusion drawn from the thesis. The present thesis contains the study of energy conversion device i.e. direct methanol fuel cell anode catalyst and energy storage device, supercapacitor. The chapters 2-4 study the synthesis, morphological, structural and electrochemical investigations of transition metal oxides (Co_3O_4 , $\text{NiCo}_2\text{O}_4/\text{NiO}$) with MXene and reduced graphene oxide (rGO) as anode catalyst in direct methanol fuel cell. Chapters 5 and 6 study the electrochemical properties of $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{rGO}$ and $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{MXene}$, respectively as supercapacitor electrode. The key findings and the future prospects of the thesis are outlined below:

7.1 Conclusions:

1. As a contender of the traditional noble metal based direct methanol fuel cell anode catalyst, a non-noble metal based anode catalyst is developed. Spinel Co_3O_4 nanoparticles are decorated over two-dimensional Ti_3C_2 MXene nanosheets. The mesopores of the nanocomposite $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$ allow easy ion penetration and make the active sites more accessible to the ions, leading to enhanced electrode-electrolyte interactions. The hybrid nanosystem $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$ minimizes the agglomeration of the metal oxide, Co_3O_4 nanoparticles and restacking of MXene nanosheets, thereby offering a greater surface area for Co_3O_4 dispersion, leading to shorter ion diffusion pathways. The hydrophilic terminations of MXene help in developing strong interactions with the Co_3O_4 nanoparticles. The large surface area and the conducting network offered by the MXene nanosheets, and the strong interactions between MXene and Co_3O_4 nanoparticles lead to high surface coverage of adsorbed redox couples. The nanocomposite $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$ exhibits high methanol oxidation current density (38.38 A/g), low onset potential (0.32 V), lower Tafel slope (191 mV/dec) and lesser charge transfer resistance (7.45 Ω). The hydrophilic terminations on the surface of MXene play major role in methanol oxidation, by adsorbing more methanol molecules and recreating the active sites by releasing the adsorbed CO molecules, thereby increasing the durability of the catalyst. Formaldehyde is formed as byproduct of methanol oxidation reaction, as confirmed from the post methanol oxidation XPS spectra of $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$.

2. To enhance the conductivity of mono-metallic oxides, another mesoporous anode catalyst $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{rGO}$ is developed based on reduced graphene oxide (rGO). The layer-on-layer

morphology of the nanocomposite enhances the surface area and causes interfacial interactions among the components. The mesoporous structure facilitates faster ion transfer and more electrode-electrolyte interactions. Low conductivity and aggregation issue of transition metal oxides NiCo_2O_4 and NiO are compensated by the nanocomposite developed with conducting reduced graphene oxide. The conducting reduced graphene oxide nanosheets and the strong interfacial interactions among the components lead to higher electron transfer coefficient and heterogeneous rate constant of the nanocomposite $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{rGO}$. This leads to high methanol oxidation current density (26.86 A/g) with low onset potential (0.32 V vs Ag/AgCl). Numerous electroactive sites, conducting network created by reduced graphene oxide causes low charge transfer resistance of the nanocomposite. Low Tafel slope, low deterioration rate constant and 65.63% current retention after 1000 CV cycles reflect better stability and durability of the nanocomposite $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{rGO}$. Few intermediate products namely formaldehyde, formate, methoxy are expected from the post methanol oxidation FTIR and XPS results.

3. As a potential competitor of reduced graphene oxide, MXene is explored as conducting two-dimensional support for $\text{NiCo}_2\text{O}_4/\text{NiO}$ as anode catalyst in direct methanol fuel cell. The nanocomposite $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{MXene}$ (CNOT) offers several benefits such as unique combination of hydrophilicity and conductivity of MXene, large surface area of MXene, numerous redox active sites due to presence of NiCo_2O_4 and NiO . Moreover, the symbiotic dependence of NiCo_2O_4 , NiO and MXene aid in retaining the structure without agglomeration of the transition metal oxides and restacking of MXene nanosheets. The mesopores on its structure help in better ion penetration and increases electrode-electrolyte interactions, providing reversibility to the system. The hydrophilic terminations -O, -F, -OH present on the surface of MXene act as sites for interfacial interactions with the transition metal oxides, and this interaction facilitates more charge transfer within the nanocomposite. The ion transfer pathways also get shortened by such good interfacial interactions and lead to high heterogeneous rate constant of the nanocomposite. Due to the synergistic effect of the individual components, $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{MXene}$ exhibits both surface adsorbed and diffusion-controlled reaction mechanisms and offers good methanol catalysis. The nanocomposite $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{MXene}$ outperforms many graphene-based catalysts by achieving 67% current retention after an hour of methanol oxidation. CNOT offers lower Tafel slope and lesser deterioration rate than CNOG, which suggests better durability of MXene based catalyst

(NiCo₂O₄/NiO) than rGO. The hydrophilic terminations -OH present on the MXene surface contribute to such resistance towards CO intermediate, as these terminations adsorb CO to form CO₂, thereby releasing the active sites. Formaldehyde, formate, methoxy, and dimethyl carbonate are some of the intermediate products identified by post catalysis spectroscopic results. The loss of the layered structure of MXene nanosheets and change in morphology of NiCo₂O₄/NiO/MXene to some block like structure reduces the surface area and ion access to active sites, which lessens the catalytic activity of the nanocomposite.

4. NiCo₂O₄/NiO/rGO (CNOG) presents itself a potential supercapacitor electrode. The mesopores of the nanocomposite and the variable oxidation states of Ni and Co lead to enhanced specific capacitance of the nanocomposite. The layer-on-layer structure of the nanocomposite NiCo₂O₄/NiO/rGO offers optimal surface area by minimizing restacking and agglomeration of MXene nanosheets, NiCo₂O₄ nanoflakes and NiO nanoparticles respectively. Due to the pseudocapacitive components NiCo₂O₄ and NiO, NiCo₂O₄/NiO binary electrode has low stability, which is compensated in the nanocomposite NiCo₂O₄/NiO/rGO by the presence of rGO nanosheets. On the other hand, the nanocomposite NiCo₂O₄/NiO/rGO exhibits higher capacitance and energy performance due to the presence of pseudocapacitive component, NiCo₂O₄ and NiO. Thus, the synergistic contribution from each component improves the performance of the hybrid electrode NiCo₂O₄/NiO/rGO. The symmetric supercapacitor device designed using PVA-KOH hydrogel polymer electrolyte outshines the aqueous electrolyte based symmetric supercapacitor by providing wider potential window of 1.3 V. The symmetric supercapacitor CNOG//CNOG in aqueous 3 M KOH offers a specific capacitance of 59.48 F/g at 1.5 A/g, whereas, CNOG//CNOG in PVA-KOH hydrogel exhibits specific capacitance of 88.8 F/g, energy and power density being 20.84 Wh/kg and 1003 W/kg respectively at 1.5 A/g. At higher current density of 10 A/g, specific capacitance of 32.63 F/g is obtained. It offers 54.10% capacitive retention after 4500th GCD cycles by maintaining 90.23% coulombic efficiency. Four such cells in series can glow a 1.8 V light-emitting diode for around 30 seconds.

5. NiCo₂O₄/NiO/MXene (CNOT) proves itself a promising supercapacitor electrode. As potential contender of graphene, MXene proves its versatility in energy storage and conversion devices with its unique properties of conductivity, hydrophilicity, and large surface area. The mesopores of the nanocomposite NiCo₂O₄/NiO/MXene facilitate easier and faster access of the

electroactive sites. The hydrophilic terminations of MXene develop strong interfacial connections with the pseudocapacitive components NiCo₂O₄ and NiO which results in enlarged surface area and increased charge transfer due to reduction in ion transfer pathways. The restacking of MXene nanosheets are minimised in the nanocomposite due to the presence of NiCo₂O₄/NiO. Thus, the synergistic contribution of MXene and pseudocapacitive NiCo₂O₄ and NiO improves the performance of the nanocomposite NiCo₂O₄/NiO/MXene. The symmetric supercapacitor CNOT//CNOT developed in aqueous KOH electrolyte provide 0.9 V potential window and exhibits specific capacitance of 32.66 Fg⁻¹ at 2.5 A/g. The symmetric supercapacitor device designed using PVA-KOH hydrogel electrolyte offers a broader window of 1.4 V with high specific capacitance of 87.331 Fg⁻¹, energy and power density of 23.77 Wh/kg and 1808.87 W/kg at 2.5 A/g respectively. It offers coulombic efficiency and capacitance retention of 90.96% and 64%, respectively, at 10 A/g current density. The hydrogel polymer electrolyte outperforms the aqueous electrolyte by providing wider potential window, higher specific capacitance and energy, power density. Four hydrogel based symmetric cells in series can glow a 1.8 V led light for more than two minutes.

7.2 Future prospects

The thesis work is focused on development of two-dimensional material-transition metal oxide based electroactive material for direct methanol fuel cell anode catalyst and supercapacitor. Some of the future prospects of the thesis are as follows:

- 1) Different two-dimensional materials like Transition Metal Dichalcogenides, different MXenes, etc. can be explored.
- 2) Different nanostructures of Transition Metal Oxides can be studied.
- 3) Different acidic and neutral electrolytes can be explored to study the catalytic and supercapacitive behavior differences.
- 4) In situ spectroscopic studies can be performed to monitor the reaction processes occurring in the electrode and electrode-electrolyte interface.
- 5) DMFC device performance can be studied using the developed electrodes.