

Abstract

With the current situation of global energy crisis, researchers are working relentlessly to develop effective energy conversion and storage technologies to replace the prevailing fossil fuels. Among the various energy conversion devices, direct methanol fuel cell (DMFC) is a potential conversion device owing to its high power density, low pollutant emissions, and high conversion efficiency. Moreover, methanol is less toxic and biodegradable fuel, its simple chemical structure does not require the breaking of C-C bond. Despite of these advantages, the methanol oxidation is a very sluggish reaction and demands the use of anode catalyst. Traditional Pt-based noble metal catalysts are state-of-the-art electrocatalyst due to their faster reaction kinetics. However, high price, unavailability and reduction in activity due to CO poisoning hinders the large-scale production of these catalysts. On the other hand, easy availability, better electrochemical stability and low cost of transition metal oxides (TMOs) make them potential replacement of the noble-metal based anode catalysts. As energy storage devices, supercapacitors have gained popularity in the market of smart grids, electrical cars, and portable electronic gadgets. Supercapacitors have a broad operating temperature range, possess high cycle life and low charging time, and act as instantaneous power supply as compared to batteries and fuel cells. Supercapacitors, also called ultracapacitors can bridge the gap between conventional capacitors and batteries and can fulfill intermediate energy requirements. Supercapacitors are divided into three categories based on their charge storage criteria; they are: (i) Electric double layer capacitor (EDLC), (ii) Pseudocapacitor, and (iii) Hybrid supercapacitor. EDLC store charge electrostatically and no faradaic reactions take place, as a result it provides high power density and long cycle life. Whereas in pseudocapacitor, charge storage takes place faradaically by transfer of charge between electrode and electrolyte, thus offering high specific capacitance and low power density and cycle life. Hybrid supercapacitor combines the EDLC and pseudocapacitance in one, thereby mitigating the individual weaknesses of each storage mechanism. Thus, development of hybrid electrode can solve the problem of low energy density of supercapacitor without compromising the power density.

High performance of these supercapacitor and anode catalyst electrodes are dependent on electrode properties namely, specific surface area, porosity, hydrophilicity, conductivity, interfacial contact, ion diffusion pathway, concentration of surface-active sites, stability, etc. Pondering these points, the present thesis investigates different

nanocomposites of transition metal oxides and two-dimensional material reduced graphene oxide and MXene as direct methanol fuel cell anode catalyst and supercapacitor electrode. The multiple oxidation states of transition metal oxides act as redox active sites and endow them with rich electrochemistry. However, transition metal oxides suffer from low conductivity and aggregation, which can be compensated by developing nanocomposites with conducting two-dimensional materials. Large surface area, outstanding electronic properties, excellent mechanical strength and flexibility of two-dimensional materials endow them with multiple functionalities. Thus, two-dimensional materials and their nanocomposites offer large effective surface area and better electrochemical properties by preventing the agglomeration of the transition metal oxides.

Chapter 1 describes briefly the direct alcohol fuel cells, working principle and classifications. Direct methanol fuel cell is discussed briefly with different components explained. Applications of DMFCs are discussed followed by challenges pertaining to it and scope of improvement. The chapter continues with a brief description of supercapacitors, working principle, merits and demerits followed by scope of improvement. The different materials studied in the thesis are also discussed in this chapter. Towards the end of the chapter, scope of the thesis and statement of thesis problem have been mentioned.

Chapter 2 presents the development of non-noble metal, spinel Co_3O_4 nanoparticles decorated over two-dimensional Ti_3C_2 MXene nanosheets as anode catalyst for methanol oxidation. The porous nanocomposite $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$ is synthesized using simple hydrothermal method. The hybrid nanosystem $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$ reduces the agglomeration of Co_3O_4 nanoparticles and restacking of MXene nanosheets, which offers a larger surface area for Co_3O_4 dispersion, leading to shorter path for the charge carriers. $\text{Ti}_3\text{C}_2/\text{Co}_3\text{O}_4$ exhibits methanol oxidation current density of 38.38 Ag^{-1} which is 2.9 times higher than that of $\text{Co}_3\text{O}_4/\text{GC}$ in 1.5 M methanol. The hydrophilic terminations on the surface of MXenes create strong interactions with the Co_3O_4 nanoparticles and act as adsorption sites for methanol molecules, leading to increased methanol oxidation reaction of the nanocomposite. A low onset potential (0.32 V), high oxidation current density of the nanocomposite, efficient durability and cycling stability (37% retention factor) up to 200 CV cycles make this nanocomposite a better alternative to the state-of-the-art noble-metal electrocatalysts.

Chapter 3 presents the development of porous non-noble metal-reduced graphene oxide (rGO) based electrode, NiCo₂O₄/NiO/rGO as anode catalyst for methanol oxidation. In-situ synthesized nanocomposite NiCo₂O₄/NiO/rGO consists of layer-on-layer structure of NiCo₂O₄ nanoflakes and rGO nanosheets, on which NiO nanoparticles are dispersed. The low conductivity and problem of aggregation of transition metal oxides are overcome by developing the nanocomposite of NiCo₂O₄/NiO with rGO. NiCo₂O₄/NiO/rGO exhibits low onset potential (0.32 V) and high methanol oxidation current density of 26.86 A/g, which is 8.5 and 17 times higher than that of NiCo₂O₄/NiO and NiCo₂O₄ respectively in 3 M methanol. The layer-on-layer morphology of NiCo₂O₄/NiO/rGO and the interfacial interactions among NiCo₂O₄ nanoflakes, NiO nanoparticles and rGO nanosheets increase the specific surface area of the hybrid, which leads to enhanced ion penetration into the active sites and provide excellent electrode-electrolyte interaction. Multiple redox sites exposed to the surface, porous electrode structure, large surface area, better electrical conductivity lead to minimum charge transfer resistance (6 Ω) of NiCo₂O₄/NiO/reduced graphene oxide. Low deterioration rate after one hour of methanol oxidation and 65.63% current retention after 1000 CV cycles, make NiCo₂O₄/NiO/rGO a durable anode catalyst.

Chapter 4 presents the development of non-noble metal based nanocomposite of NiCo₂O₄/NiO with two-dimensional Ti₃C₂ MXene nanosheets. The unique combination of hydrophilicity and conductivity of MXene, offers numerous advantages to the nanocomposite NiCo₂O₄/NiO/MXene. Low conductivity and aggregation of transition metal oxides are compensated by making hybrid of NiCo₂O₄/NiO with MXene. The mesopores present on hybrid NiCo₂O₄/NiO/MXene provide easy insertion of electrolyte ions into the active sites, thus facilitating reversibility to the system. The hydrophilic terminations -O, -F, -OH on the surface of MXene create sites for interfacial interactions with the metal oxides. This interfacial interaction facilitates more charge transfer by increasing the specific surface area and reducing the ion transfer pathways and charge transfer resistance (4.46 Ω). NiCo₂O₄/NiO/MXene as anode catalyst for methanol oxidation offers methanol oxidation current density of 15 A/g and low onset potential (0.30 V). Low deterioration rate of $5.85 \times 10^{-6} \text{ s}^{-1}$ and 67% current retention are obtained after one hour of methanol oxidation. The hydrophilic terminations on MXene surface react with the adsorbed CO intermediates, thereby releasing the active sites. The current retention after 200 CV cycles does not change much with 25% current retention after

1000 CV cycles, which indicates good cycling stability of the catalyst NiCo₂O₄/NiO/MXene.

Chapter 5 presents the investigations of electrochemical behaviour of the nanocomposite NiCo₂O₄/NiO/rGO (CNOG) as supercapacitor electrode. The nanocomposite exhibits high specific capacitance of 854.94 F/g at 1 A/g current density with 588 F/g at 10-fold current density. Symmetric supercapacitor CNOG//CNOG offers 0.9 V as the optimum potential window and delivers specific capacitance of 59.49 F/g, energy and power density of 6.69 Wh/kg and 698 W/kg respectively at 1.5 A/g current density in 3 M KOH aqueous electrolyte. The symmetric supercapacitor offers good rate capability at 10 A/g current density and exhibits 65.9% capacitive retention after 4500 galvanostatic charge discharge (GCD) cycles. On the other hand, the symmetric supercapacitor designed using PVA/3M KOH gel polymer electrolyte allows broader potential window (1.3 V), thereby outperforming the aqueous electrolyte. The hydrogel based symmetric supercapacitor exhibits specific capacitance of 88.8 F/g, energy and power density 20.84 Wh/kg and 1003 W/kg respectively at 1.5 A/g current density with 36.75% specific capacitance at 10-fold current density. It offers 54.10% capacitive retention after 4500th GCD cycles, maintaining 90.23% coulombic efficiency. The mesoporous morphology, interfacial interaction among NiCo₂O₄ nanoflakes, NiO nanoparticles and rGO nanosheets, increased conductivity and surface area of NiCo₂O₄/NiO/rGO allow more ion movement and penetration into the electrode, further increasing its capacitance and energy density.

Chapter 6 presents the investigations of the electrochemical behaviour of nanocomposite NiCo₂O₄/NiO/MXene (CNOT) as supercapacitor electrode. NiCo₂O₄/NiO/MXene exhibits high specific capacitance of 674 Fg⁻¹, which is 26-fold higher than pristine MXene at 1 A/g current density, maintaining 63.52% capacitance retention at 10 A/g current density. The nanocomposite offers excellent cycling stability with 98.36% capacitive retention after 5500 GCD cycles. The synergistic contribution from each individual component and the interfacial interactions among them lead to enhanced performance of NiCo₂O₄/NiO/MXene as supercapacitor electrode. Symmetric supercapacitor CNOT//CNOT in 3M KOH aqueous electrolyte provides 0.9 V potential window and 32.66 Fg⁻¹ specific capacitance at 2.5 A/g. It offers excellent capacitive retention of 94% after 4500 GCD cycles. Additionally, the symmetric supercapacitor CNOT//CNOT in PVA/3M KOH gel polymer electrolyte provides a broader potential

window 1.4 V, thereby increasing the specific capacitance, 87.33 Fg^{-1} at 2.5 A/g current density. It maintains 90.96% capacitance retention even at 10 A/g current density. The PVA/3M KOH hydrogel based symmetric supercapacitor CNOT//CNOT offers high energy and power density of 23.77 Wh/kg and 1808.87 W/kg respectively at 2.5 A/g. It provides 47.9% capacitive retention after 4500 GCD cycles, maintaining 77.13% coulombic efficiency. Thus, the hydrogel based symmetric supercapacitor outperforms the aqueous 3M KOH by providing larger potential window, higher capacitance, rate performance, excellent energy and power density.

Chapter 7 summarizes the conclusions drawn from each chapter. This chapter also outlines the future prospects of the thesis work.