

Nanocomposites of Carbon as Electrocatalyst



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Abstract Earnest efforts in developing electrochemical energy production, conversion, and storage devices to meet the energy requirements globally routes to the research and development of highly efficient and sustainable electrocatalysts. The escalated physicochemical characteristics and ease in tunability of carbon material and its allotropes (viz., graphene, graphite, carbon nanotubes, carbon quantum dots, nano diamond, etc.) facilitated to exercise of its remarkable footprints in the electrocatalytic applications. Due to the trade-off between its conductivity and intrinsic activity, carbon materials are often combined with several metal oxides, sulfides, nitrides, or carbides and form their respective composites. In addition to their enhanced conductivity and stability, carbon nanocomposites will exhibit higher catalytic activity due to their higher surface-to-volume ratio which is crucial for an electrocatalyst. In this chapter, several carbon nanocomposites electrocatalysts used in water splitting (OER, ORR and HER), fuel cells (methanol and proton exchange membrane) and air batteries (lithium and zinc) applications are majorly discussed.

Keywords Carbon allotropes · Energy conversion and production · Water splitting · Air batteries · Fuel cells

1 Introduction to Electrocatalyst

The electrochemical energy sector gained significant interest over decades owing to the demand for sustainable and renewable energy devices. Electrocatalysts are indispensable entities in electrochemical energy devices. The catalysts involved in the electrochemical reactions are called electrocatalysts. The electrocatalysts are responsible for a number of electrochemical applications such as oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) in water splitting [1], carbon dioxide reduction reaction (CRR) [2], lithium and zinc air batteries [3, 4], methanol and proton exchange membrane fuel cells [5,

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6]. In the electrochemical process, the electrocatalysts are usually electrodes that are involved in facilitating the charge transfer reactions and chemical transformations carried either at their surfaces or interfaces. Mainly, the electrocatalysts decrease the activation energy of the charge transfer reaction, thereby improving the reactivity of the electrochemical process. Nanomaterials play a vital role as an efficient electrocatalyst owing to their higher surface-to-volume ratio leading to larger reactivity, efficient interfacial activity, higher adsorption and desorption of ions, improved rate of reaction etc. Several class of nanomaterials viz., metal oxides, sulphides, nitrides, carbides, metal free catalysts and noble metals are largely explored towards electrocatalyst applications. Majority of the studies proved that carbon-based materials integrated to the above class of nanomaterials or standalone carbon-based materials (viz., graphene oxides, carbon quantum dots, carbon nanotubes etc.) are highly regarded as electrocatalyst and provided significant performance in electrochemical process.

2 Carbon Based Electrocatalyst

Right from the first industrial revolution carbon acts as an integral part in the materials development in various streams of energy sector. Carbon nanomaterials exhibits in various allotropic forms namely graphite, graphene, quantum dots, nanotubes, nano diamond and various forms such as porous carbon, activated carbon, etc. and is applied in various applications as shown in Fig. 1. The characteristics of carbon based materials such as its electrical conductivity, chemical stability in alkaline and acidic medium, highly abundant, thermal stability, high durability, cost effective and less toxic makes it well suitable for electrocatalyst [7]. The noble metals such as ruthenium, platinum and iridium were used as an efficient electrocatalysts until the discovery of the carbon electrocatalysts. The exploration of carbon and carbon composite electrocatalyst replaced the expensive noble metal based electrocatalysts retaining its electrocatalytic efficiency that is suitable for large scale employability. The carbon based electrocatalysts improve the kinetics of the reaction thereby increasing the reactivity of the electrochemical process.

2.1 Graphite

The chemical and electronic properties of the carbon nanomaterials can be very well tuned by doping the heteroatoms such as boron, nitrogen, and oxygen into its graphitic network. The doping also helps in altering the electronic distribution in g-C₃N₄ [8]. The limitation of graphite are its intercalation kinetics and surface passivation which could be tackled by making it as nanocomposite with other materials. The surface functional groups of graphite acts as a key role in improving the catalytic activities [9].

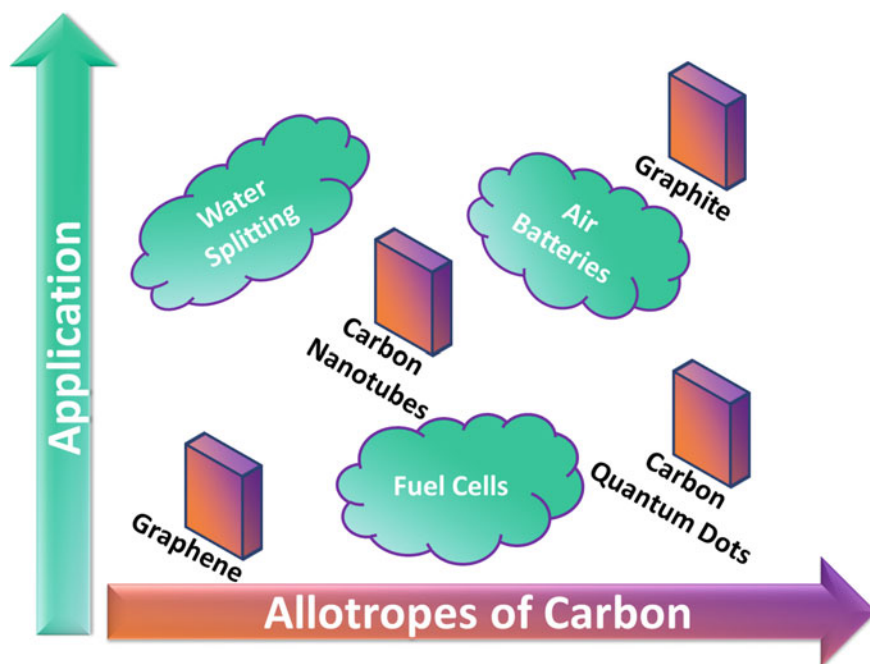


Fig. 1 Schematic representation of carbon electrocatalyst and its applications

2.2 Graphene

The invention of graphene revolutionized the materials research and development for several applications due its characteristic functional properties. Graphene, an allotrope of carbon, atomically thin sheets of carbon, having C–C bond length of $\sim 1.42 \text{ \AA}$ exhibits tremendous outstanding properties such as flexibility, electronic properties, ultra-thin structure and so on [10]. Graphene is one of the potential electrocatalysts boosting electrochemical reactions. Graphene can be well defined as carbon atoms with sp^2 hybridization in a hexagonal framework with two-dimensional sheet structure. In other words, the exfoliated graphite sheets render graphene sheet. By stacking, rolling and wrapping process graphene can be converted to 3D, 1D and 0D structures [11]. Due to its excellent physical characteristics, graphene is employed as electrocatalyst for various application and its significance as electrocatalyst have been reviewed by N. Shaari et al. [7]. The types of graphene-based material are shown in Fig. 2a.

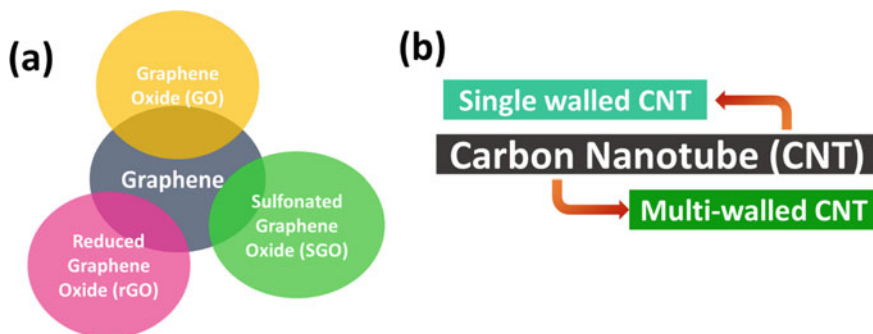


Fig. 2 **a** Types of graphene-based materials, **b** Types of carbon nanotubes

2.3 Carbon Nanotubes

Carbon nanotubes are 1D nanostructures with the length being in few micrometres with nanoscale tube diameter. The types of carbon nanotubes are given in Fig. 2b. The geometry of carbon nanotubes is distinctive that are bonded by sp^2 carbon-carbon chemical bonds. Gedefaw Asmare Tafete et al., reported the works of carbon nanotube electrocatalyst in detail. The structural uniqueness of carbon nanotubes provide enhanced electronic conductivity, mechanical and chemical stability [12].

2.4 Carbon Quantum Dots

The carbon quantum dots are zero dimensional unique quasi spherical nanoparticles of size less than 10 nm. They have better surface properties with π - π stacking, higher surface area, higher crystallization and larger diameter, higher solubility, robustness, and chemical inertness. In energy conversion applications, graphene quantum dots are widely used usually with heteroatom doping enhancing oxidation and reduction reactions. Graphene quantum dots are usually less than 30 nm in size having few atomic layer thickness and mainly used in luminescence applications [11].

3 Carbon Nanocomposites

Due to its outstanding properties, carbon-based materials are often incorporated with several class of materials including metals, metal oxides, metal organic frameworks etc. Due to its higher surface to volume ration influencing the surface activity and conductivity carbon-based materials are largely employed in electrocatalytic applications. Applications involving carbon-based electrocatalyst, mainly energy storage and conversions are discussed in this chapter.

4 Applications

Electrocatalyst is the major element in an electrochemical process and it acts as an electrode. Depending on the applications, electrocatalyst acts either as anode or cathode. The electrochemical activity occurs either at surface or interfaces of the electrodes. They can be either homogeneous such as platinum or heterogeneous material. A brief study on the applications involving electrocatalyst such as water splitting (OER, ORR and HER), fuel cells (methanol and proton exchange membrane fuel cells) and batteries (zinc air, lithium air and lithium-ion batteries) are discussed in this chapter.

4.1 Water Splitting

Hydrogen economy is at the growing phase due to its scope of green energy production from water. Water splitting is one of the wonders in the chemistry which opened a wider path towards renewable energy production eliminating fossil fuels. Oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) are major reactions that need to be realized and improved for a better performance water splitting. The electrocatalysts plays a major role in deciding the efficiency of the electrochemical reactions involved in water splitting reaction.

4.1.1 Oxygen Evolution Reaction (OER)

OER, four electron transfer reaction occurring at anode with sluggish kinetics is one of the biggest challenges in electrochemical water splitting. Hence, a material with higher electronic conductivity and charge transport characteristics are preferred to be an OER electrocatalyst. In that row, several single and mixed metal oxides are employed in water splitting application. In addition, reports suggest that incorporating carbon-based materials with metal oxides will compliment metal oxides in improving the surface area, influencing the catalytic activity etc.

Fengcui shen et al., studied the catalytic activity of $\text{CoV}_2\text{O}_6\text{-V}_2\text{O}_5/\text{N-doped rGO}$ synthesized by direct carbonization of its precursors towards OER. The $\text{CoV}_2\text{O}_6\text{-V}_2\text{O}_5/\text{N-doped rGO}$ nanocomposite was coated on glassy carbon electrode which acts as working electrode and its electrocatalytic activity was studied in 1 M KOH saturated using nitrogen. The studies revealed that $\text{CoV}_2\text{O}_6\text{-V}_2\text{O}_5/\text{N-doped rGO}$ nanocomposite required an overpotential of 239 mV at the current density of 10 mA cm^{-2} . The Tafel slope value (49.7 mV dec^{-1}) of $\text{CoV}_2\text{O}_6\text{-V}_2\text{O}_5/\text{N-doped rGO}$ nanocomposite which is lower than other compared electrocatalysts in this work revealed that indicates exhibits better reaction kinetics due to its faster charge transport and improved surface area. The cyclic stability was observed for over 1000 cycles at the scan rate of 100 mV/s in the potential 1.3 and 1.5 (V versus

RHE). The durability of the $\text{CoV}_2\text{O}_6\text{-V}_2\text{O}_5/\text{N-doped rGO}$ nanocomposite was also confirmed using chronoamperometry. The turnover frequency (TOF) was found to be 1.80 s^{-1} representing the better performance of the electrocatalyst. Therefore, this work proved that $\text{V}_2\text{O}_5/\text{N-doped rGO}$ nanocomposite as an excellent electrocatalyst for OER with higher TOF and lower overpotential [13].

Xiaolin Xing et al., studied the OER as well as ORR performance of manganese vanadium oxide–N-doped reduced graphene oxide ($\text{MnVO}_x@ \text{N-rGO}$) composite synthesized using hydrothermal synthesis. The OER studies were studied using linear sweep voltammetry and electrochemical impedance spectroscopy by coating $\text{MnVO}_x@ \text{N-rGO}$ on carbon fibre paper in 1 M KOH. The $\text{MnVO}_x@ \text{N-rGO}$ nanocomposite rendered an overpotential of 1.65 V at 10 mA/cm^2 with Tafel slope value of 271 mV. The over-all oxygen activity was determined by finding the potential difference ($\Delta E_{\text{OER}} - \Delta E_{\text{ORR}}$) between OER and ORR potential at the current density of 10 mA/cm^2 . The $\text{MnVO}_x@ \text{N-rGO}$ yielded $\Delta E_{\text{OER}} - \Delta E_{\text{ORR}}$ value of 0.85 V versus RHE. This minimum potential difference implies the better oxygen activity of the $\text{MnVO}_x@ \text{N-rGO}$ catalyst [14].

Hybrid electrocatalysts plays a significant role in improving the electrochemical efficiency due to its synergistic effects. Several reports on electrocatalysts involving more than two materials are found in literature which emphasize on the individual material's advantages complimenting the composite.

A work on two step gas phases synthesized $\text{Co}_3\text{O}_4\text{-MnO}_2\text{-CNT}$ nanocomposite as OER electrocatalyst was reported by Kungeng Xie et al. As the metal oxides limits the conductivity compared to noble metals, usually carbon- based materials are incorporated with metal oxides to improve the conductivity and reduce the charge transfer resistance as well. In this work, $\text{Co}_3\text{O}_4\text{-MnO}_2\text{-CNT}$ nanocomposite was treated with nitric acid (HNO_3) at $200 \text{ }^\circ\text{C}$ and the electrochemical characteristics were studied. The $\text{Co}_3\text{O}_4\text{-MnO}_2\text{-CNT}$ nanocomposite exhibited good catalytic performance at the current density of 10 mA/cm^2 and the cyclic stability was found over a period of around 37 h. This work proved that employing $\text{Co}_3\text{O}_4\text{-MnO}_2\text{-CNT}$ nanocomposite as electrocatalyst would yield a scalable electrode helping large scale production [15].

4.1.2 Hydrogen (H_2) Evolution Reaction (HER)

The ardour for electrochemical water splitting research is purely for H_2 production to enable green energy society. For several decades, splitting H_2O into H_2 and O_2 is prevailing using electrolysis method. But developing a method suitable for large scale production, low cost and environmentally safe procedures are challenging and hence still research is moving towards developing the same. Though metal oxide possesses several advantages in terms of its availability, cost, nanostructured morphology, stability and better catalytic behaviour, its wider band gap limits its electronic conductivity. Hence, usually carbon-based materials are incorporated with metal oxides to increase the electrocatalytic activity of the material. The HER is a cathodic reaction in the water electrolysis reaction. In their work, Bishal Das et al.,

reported photocatalytic hydrogen evolution reaction of metal complex (VO (acac)₂) and dual (sodium and sulfur) doped graphitic carbon nitride (VNS-GC). The VNS-GC composite exhibited a hydrogen evolution rate of 310.63 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in the presence of platinum co-catalyst. The results support the better cyclability as well as photoactivity of the metal complex/carbon composite [16].

Yanping Zhu et al., reported one pot synthesis of tungsten nitride and nitrogen-rich graphene-like carbon nanocomposite (WN-NRC) that are hierarchically arranged and employed it as an electrocatalyst for HER. The electrochemical characteristics of WN-NRC was studied in a three-electrode system in 0.5 M H₂SO₄. From linear sweep voltammetric studies, it was found that WN-NRC exhibited an overpotential of 255 mV at 10 mA cm⁻², which is very much less compared to its bulk counterpart which had an overpotential of 492 mV. It shows that the nanocomposites of WN-NRC are excellent catalyst for HER due to its increased active sites. In addition, the counter electrode also plays a vital role in deciding the electrocatalytic activity of the catalyst. In this work, the catalytic activity of WN-NRC was found to be high when platinum counter electrode was used compared to the graphite rod counter electrode. The charge transfer resistance (R_{CT}) observed from electrochemical impedance spectroscopy indicated that the R_{CT} value of WN-NRC is lower due to its porous morphology than its bulk particles. The work provides a rational for scalable synthesis of WN-NRC and its application as electrocatalyst in hydrogen evolution reaction [17].

4.1.3 Oxygen Reduction Reaction (ORR)

The ORR is a crucial process in electrochemical conversion process such as fuel cells and batteries. Deshuang Yu et al., reported metal organic framework (MOF) based electrocatalyst cobalt nano- particles encapsulated in nitrogen-doped carbon and carbon nanotube (Co/N-CCN) for ORR application as well as its employability for OER. The ORR characteristics of Co/N-CCN was studied using rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) in 0.1 M KOH. The RDE study showed that the Co/N-CCN exhibited onset potential and half wave potential of 0.924 and 0.81 V respectively. The better efficiency of Co/N-CCN towards ORR is due to the presence of active pyridine-N and graphitic-N in the MOF and carbon nanotube network. The work also supports the use of Co/N-CCN composite in Zn-air battery applications [18].

Yu Pan et al., reported the electrochemical characteristics of palladium/iron nanoparticles supported by carbon towards ORR. Usually, noble metals are better catalytic agents in electrochemical studies. That way, Pd plays a huge role in the catalytic performance. In addition to catalytic activity, the conductivity and reduction in overpotential are the major factors to support the electrocatalysis. In this work, the addition of iron to the palladium decreased the overpotential of the composite and the carbon improved he charge transfer due to its surface properties. The consistency of the electrocatalyst was studied using linear sweep voltammetry where even

after 50 scans, the trend remained same showing the stability and durability of the electrocatalyst [19].

4.2 Fuel Cells

The fuel cells play an important role in meeting energy demands in global arena. Basically, fuel cells convert chemical to electrical energy in an electrochemical process. There are several types of fuel cells such as alkaline, phosphoric acid, molten carbonate and solid oxide fuel cells in addition to methanol and proton exchange membrane fuel cells. In this chapter, the carbon-based nanocomposites employed as electrocatalyst in methanol and proton exchange membrane fuel cells are discussed.

4.2.1 Methanol Fuel Cells

The demand for sustainable and clean energy sources has led to the development of research and development in methanol fuel cells. To commercialize methanol fuel cells as an efficient energy source, its expensive applicability due to the use of platinum anode and sluggish kinetics remains as its challenging factor. To overcome this, research on carbon-based materials and its composites are widely studied in recent times which possess good electrocatalytic activity, higher surface to volume ratio and better stability during chemical reactions. An extensive discussion on the progress and challenges in carbon-based materials (mesoporous carbon, carbon black, carbon nanofibers, carbon nanotubes, graphene) as anodes for methanol oxidation reaction was reported by Huajie Huang et al. [20].

In addition to these major carbon materials, other carbon materials such as carbon aerogel and carbon paper were also studied as an electrocatalyst towards ethanol oxidation reaction for the fuel cells applications. The materials such as nitrogen doped carbon, CeO_2 , MnO_2 , TiO_2 and conducting polymers such as polyaniline and poly(2-amino-5-mercapto-1,3,4-thiadiazole) are studied largely as an efficient co-catalyst of carbon for methanol oxidation reaction. B. Rajesh et al., reported Pt- WO_3 /carbon nanotube composite for the methanol oxidation in acidic medium. Self-poisoning due to CO production at the time of dehydrogenation remains a challenging task in selecting the anode catalyst in the methanol oxidation reaction. Hence, this work reports that the Pt/ WO_3 provides better stability during the catalytic reaction of methanol oxidation. But Pt/ WO_3 lower activity in the catalytic reaction. Hence, in this work, Pt/ WO_3 were loaded inside carbon nanotubes and CNT/Pt- WO_3 coated on glassy carbon electrodes were used for electrochemical studies towards methanol oxidation reaction. In the forward scan, at room temperature condition, the methanol oxidation onset potential started at + 0.1 V and higher current density of 98.5 mA/cm² was obtained at + 0.7 V versus Ag/AgCl without any self-poisoning at the reverse scan. Zhenyu Sun et al., reported the methanol oxidation electrochemical performance of Pt-Ru/ CeO_2 /multiwalled carbon nanotube composite. In this work,

the Pt-Ru/CeO₂ were attached to the surface of multiwalled carbon nanotube through sonication method. The electrochemical characteristics of Pt-Ru/CeO₂/multiwalled carbon nanotube composite towards methanol oxidation were studied using cyclic voltammetry and chrono-amperometry in 0.5 M H₂SO₄. The electrochemical surface area of Pt-Ru/CeO₂/MWNT (122.4 m² g⁻¹) was found to be higher than Pt-Ru/MWNT (77.4 m² g⁻¹) and Pt/MWNT (36.6 m² g⁻¹). From chrono-amperometric studies, it was found that the oxidative current of the Pt-Ru/CeO₂/MWNT nanocomposite was higher than the Pt-Ru/MWNT and Pt/MWNT inferring that the methanol oxidation reaction was better for Pt-Ru/CeO₂/MWNT than other catalysts [5].

Yuehe Lin et al., reported an interesting work on low temperature fuel cells using Pt/CNT synthesized in supercritical fluid. The self-poisoning of the electrodes occurring in the middle of the methanol oxidation reaction can be understood using the difference between forward (I_f) and reverse anodic peak current (I_b). Higher the I_f/I_b value, better the methanol oxidation to CO₂. This work suggested that the use of CNT with Pt reduced the catalyst poisoning as well as increased the surface activity due to the increased surface area of CNT and decrease in overpotential [21].

4.2.2 Proton-Exchange Membrane Fuel Cells (PEMFC)

In a view to develop eco-friendly energy sources, research on PEMFC is on a larger interest in global arena. The PEMFC consists of an anode where the hydrogen will be oxidized and a cathode where the oxygen will be reduced and an electrolyte membrane. The proton is migrated from anode to cathode through proton exchange membrane. There are two types of PEMFC depending on the temperature namely low temperature PEMFC (60–80 °C) and high temperature PEMFC (110–180 °C). The high temperature PEMFC provides higher proton conductivity with better chemical and thermal stability. In addition, high PEMFC also offers low permeability towards fuel and carbon monoxide poisoning occurring at low temperature PEMFC is controlled in high PEMFC. To overcome its lower power density limitation in PEMFC, focus on developing efficient catalyst is believed to deliver better performance. Platinum is the ideally used catalyst for PEMFC applications. But, due to its cost and availability as well as poisoning limitations, Pt is often supported by carbon-based materials. Hence, recently carbon based electrocatalyst is studied at a larger scale to enhance the PEMFC performance. The Pt/C also delivers attractive electrocatalytic activity improving the cell performance. Among various carbon-based materials, carbon nanotubes (CNT) are majorly used for PEMFC application owing to its nanoscale morphology, higher surface area, better stability and corrosion resistance in addition to higher electrical conductivity. Both single wall and multi walled CNTs exhibit higher surface area improving the electrochemical activity.

Weimin Zhang et al. studied the electrocatalytic performance of Pt/CNT nanocomposite synthesized using microwave heating towards PEMFCs. The CNT were functionalized and the difference in electrocatalytic performance of raw and functionalized CNT were studied. The Pt/CNT electrodes with functionalized CNT exhibited an electrochemical active surface area of 72.9 m²/g and the Pt/CNT electrodes with

unfunctionalized CNT exhibited an electrochemical active surface area of $48.2 \text{ m}^2/\text{g}$. This shows that the CNT electrodes which are functionalized possess better catalytic activity towards proton membrane exchange fuel cells [22].

A. Leela Mohana Reddy et al., reported electrochemical performance of Pt/SWNT (single wall nanotube)–Pt/C (carbon) nanocomposite towards PEMFC. The enhanced electrochemical performance of Pt/SWNT–Pt/C was found when 50 wt % Pt/SWNT + 50 wt % Pt/C was taken as both anode and cathode where 20% of Pt was loaded. The uniform distribution of Pt/C over Pt/SWNT was observed in this study using transmission electron microscopy. The PEMFC performance with a potential of 540 mV exhibited a current and power density of 485 mA cm^{-2} and 262 mW cm^{-2} . The performance of Pt/SWNT was found to be better than Pt/C indicating the advantages of SWNT. The membrane with thickness of $89 \text{ }\mu\text{m}$ exhibited a membrane resistance of $0.1072 \text{ }\Omega \text{ cm}^2$. The study exhibited Pt/SWNT as a better cathode catalyst than Pt/C with enhanced electron transfer and higher catalytic activity [6]. In addition to being an electrocatalyst, carbon/chromium composite coating as bipolar plates in PEMFC yielded better interfacial conductivity as well as anticorrosive property. Elisabete I. Santiago et al., reported the use of PtMo/C composite as electrocatalyst for PEMFC. The Mo/C diffusion layer helped in lowering the CO concentration in the electrodes hence promoting the CO tolerance of PtMo/C composite. The performance of Mo/C in reducing the CO concentration was also confirmed using gas chromatographic technique [23].

4.3 Batteries

4.3.1 Lithium Air (Li-Air) Batteries

Littauer and Tsai introduced lithium air batteries in the year 1976. Due to its higher theoretical energy density Li-O₂ batteries are considered as a good choice for electrochemical power source. For a material to exhibit better electrochemical performance towards Li-O₂ battery must be exhibit a better catalytic activity towards ORR. In that case, noble metals like platinum (Pt), usually exhibit effective ORR activity. As the noble metals as ORR catalyst are expensive and challenging to employ in real-time, carbon-based materials plays a vital role as its alternative. Oi Lun Li discussed the challenges and prospects in using carbon electrodes towards lithium air battery applications. The role of electrolyte (aqueous, non-aqueous, hybrid (aqueous/non aqueous) and solid electrolytes) also plays an important role in the functioning of the electrocatalyst. Carbon materials are often used as cathode in Li-air batteries where the cell voltage drop occurs [4].

Co₃O₄ doped hollow carbon nanospheres were grown in-situ by Wang et al., and employed it for lithium-air battery application. Co₃O₄/nitrogen-doped hollow carbon nanospheres was used as air electrode in coin type Li-O₂ battery. The incorporation of Co₃O₄ into carbon composite are believed to reduce the overpotential and improve catalytic activity. The carbon nanospheres used in this works supports

electron mobility as well as develops nucleation sites for the transition metal oxides. The synthesized Co_3O_4 /nitrogen-doped hollow carbon nanospheres exhibited mesoporous structures with the surface area of $278.3 \text{ m}^2\text{g}^{-1}$ helping faster transport of oxygen and increasing the reactivity supporting the discharge reactions. The specific discharge capacity of the nanocomposite was about 3325 mAhg^{-1} . The work also discussed the limitation of the cyclic stability of the synthesized nanocomposite. Hence, by improving the stability and optimizing the electrode efficient air-batteries as bifunctional catalysts can be achieved [24].

The electrochemical performance of $\delta\text{-MnO}_2$ /N-rGO towards the studies on Li-O_2 battery was discussed by Awan Zahoor et al. The porous nature, higher theoretical energy density, abundance, ease in ion transportation makes MnO_2 as a better electrocatalyst to be used in Li-O_2 battery application. In this work, the battery specific capacity of $\delta\text{-MnO}_2$ /N-rGO nanocomposite was found to be 5250 mAhg^{-1} . The $\delta\text{-MnO}_2$ /N-rGO electrodes also exhibited better discharge capacity of 3300 mA h g^{-1} at 0.1 mA cm^{-2} . The N-graphite species combined with $\delta\text{-MnO}_2$ in this work acted as a better ORR catalyst with improved reaction kinetics and energy conversion efficiency [25]. Masoumeh Salehia et al., studied the effect of rGO/CNT nanocomposite with specific surface area of $564.48 \text{ m}^2/\text{g}$ as electrocatalyst for Li-air batteries application. The work yielded better cyclability for about 50 cycles and at 100 mA/g it delivered the capacity of 9000 mA h/g . At 50 mA/g , the discharge capacity of $12,350 \text{ mA h/g}$ is obtained. The work also employed constant current and constant current/voltage discharge method [26].

The carbon materials are usually doped using nitrogen to make it as an effective electrochemical catalyst in terms of improved electron conductivity and durability as well as surface active sites. Hence, doping carbon with nitrogen while synthesizing nanocomposites with transition metal oxides is one of the effective strategies in enhancing the electrocatalytic performance.

4.3.2 Zinc Air (Zn-Air) Batteries

Due to its high theoretical energy density and low cost than Li-air batteries research on zinc-air (Zn-air) batteries gained significant attention in energy storage applications specifically for rechargeable batteries [27, 28]. In addition, Zn based materials are highly stable, abundantly available, less toxic and cost effective. Due to its physicochemical properties, electrical conductivity and its cost-effectiveness, carbon-based materials are widely used as a bifunctional catalyst for Zn-air battery applications [29]. Daolan Liu et al. reported the recent advances in Zn-air batteries using carbon based bifunctional catalyst [3].

Qing Qin et al. reported the multifunctional catalytic activity (OER, HER, ORR and Zn-air battery) of nitrogen and phosphorous co-doped carbon-supported Fe nanocomposite prepared through one-pot pyrolysis approach. In this work, carbon has been derived from tannic acid which is highly helpful in adsorbing properties. The developed nanocomposite exhibited an overpotential of about only 75 mV at 10 mA/cm^2 towards HER catalysis. The charge and discharge voltage gap was found

to be less at longer cycles which makes this nanocomposite an ideal candidature for the Zn-air battery application [30]. Xiaopeng Han et al., reported NiCo_2S_4 /nitrogen doped carbon nanotubes as an efficient bifunctional catalyst with better performance than the ideal RuO_2 and Pt/C electrodes with lower overpotential of about 0.63 V corresponding to charge/discharge and cyclability of 150 cycles. The nitrogen doped carbon nanotubes facilitated the surface conductivity as well as adsorption [31]. Sun et al., reported the synthesis and electrochemical studies of reduced graphene oxide/carbon black/amorphous cobalt borate (rGO/CB/Co-B) nanocomposites towards rechargeable Zn-air batteries. Herein, sandwich like structure of the nanocomposite with surface area of $1052.3 \text{ m}^2 \text{ g}^{-1}$ is developed where the graphene oxide sheets are separated by cobalt borate that are densely packed. The nanocomposite exhibited minimum charge transfer resistance followed by the higher diffusion kinetics from the LSV polarization. From the Koutecky–Levich plot signified that the synthesized rGO/CB/Co-B nanocomposite exhibited four electron transfer and rGO/Co-B exhibited two electron transfer pathways with the electron transfer number of 3.93 and 2.76 respectively. It shows that the addition of carbon black in rGO/CB/Co-B nanocomposite helps in enhanced conductivity and decreases the Lewis acidity making them thermodynamically favourable. The study proved that the rGO/CB/Co-B nanocomposite is an efficient catalyst towards OER as well as ORR and hence has been taken forward as a better cathode for Zn-air battery. In the primary study, the rGO/CB/Co-B nanocomposite exhibited a steady discharge curve up to 2000 min and also the battery exhibited the power density of $\sim 76 \text{ mW cm}^{-2}$. The rechargeable Zn-air battery made up of rGO/CB/Co-B nanocomposite was stable in 124 h cycling at the current density of 10 mA/cm^2 . The room temperature synthesized sandwich rGO/CB/Co-B nanocomposite exhibited lower discharge voltage and voltage gap at charging as well as discharging proving that the carbon based electrocatalyst as a robust Zn-air battery electrode [32].

Yan et al. reported an interesting perovskite/carbon nanocomposites synthesized using gel auto-combustion method as an electrocatalyst for oxygen reduction reaction in Zn-air batteries. The synthesized $\text{La}_{0.99}\text{Mn}_{3.03}\text{C}$ nanocomposite exhibited a specific surface area of $120 \text{ m}^2 \text{ g}^{-1}$ with pore volume of $0.401 \text{ cm}^3 \text{ g}^{-1}$. The perovskite carbon composite delivered the energy and power density of $0.401 \text{ cm}^3 \text{ g}^{-1}$ and 430 mW cm^{-2} respectively with a stability along 340 h at current density of 10 mA/cm^2 [33].

4.3.3 Lithium-Ion (Li-Ion) Batteries

Due to its layered structures, vanadium pentoxide (V_2O_5) is widely used in applications involving adsorption and diffusion kinetics including sensors, supercapacitors and batteries [34, 35]. It is largely employed as cathode material in Li-ion battery application. The layered structure helps in efficient lithium intercalation and deintercalation. In addition to the advantage of layered V_2O_5 , integrating carbon-based materials will enhance the electrocatalytic performance due to its larger surface area, conductivity and chemical stability. Yifang Zhang et al., reported the

synthesis of dodecahedron-shaped carbon framework encapsulated by V_2O_5 making carbon/ V_2O_5 nanocomposites and employed it as a cathode material for lithium-ion batteries. The as-synthesized carbon/ V_2O_5 nanocomposite exhibited higher porosity with homogeneous structure. With change in calcination temperature in the synthesis process, carbon/ V_2O_5 nanocomposites exhibited varied surface morphology because of varied carbon combustion at different temperatures. The work reported better electrochemical performance of carbon/ V_2O_5 nanocomposite than pure V_2O_5 because of synergistic performance of carbon and oxide. The carbon/ V_2O_5 nanocomposite exhibited specific capacity of 121.6 mAhg^{-1} , whereas pure V_2O_5 rendered a specific capacity of only 20 mAh/g . In addition, from electrochemical impedance spectroscopy it was noticed that the charge transfer resistance (R_{CT}) of is 267.9Ω lower than V_2O_5 electrodes which exhibited the R_{CT} value of 638.8Ω . The Li^+ ions diffusion coefficient of carbon/ V_2O_5 nanocomposite was also found to be 2–4 times higher than the V_2O_5 electrodes [36].

Bin Sun et al., reported V_2O_5 nanosphere/MWCNT electrocatalyst as cathode material for Li-ion battery. In this work, V_2O_5 and MWCNT are arranged layer-by-layer with V_2O_5 having thickness of $\sim 2\text{--}3 \mu\text{m}$ and MWCNT having thickness of $\sim 1 \mu\text{m}$ and the whole stack possessed thickness of about $\sim 20 \mu\text{m}$. From cyclic voltammetric studies of V_2O_5 /MWCNT undergone a multistep reduction process corresponding to V^{+5} signifying the phase changes from $\alpha\text{-}V_2O_5 \rightarrow \epsilon\text{-}Li_{0.5}V_2O_5 \rightarrow \delta\text{-}Li V_2O_5 \rightarrow \gamma\text{-}Li_2V_2O_5$. Good reversibility of oxidation and reduction was noticed for three cycles and the galvanostatic charge/discharge cycles were also found to be consistent. The reversible capacity of about 275 mAh/g was observed after 50 cycles. The work reports that the layered structure had good stability and cyclability helping better lithiation/delithiation due to its electrostatic interaction. Hence, the layered V_2O_5 /MWCNT electrode can be used as an efficient electrocatalyst for Li-ion batteries [37]. Hongbin Zhao et al., reported the electrochemical characteristics of V_2O_5 /rGO and VO_2 /rGO and exhibited better cyclic stability and specific capacity towards Li-ion battery studies. The specific surface area of V_2O_5 /rGO and VO_2 /rGO were found to be $64 \text{ cm}^2/\text{g}$ and $35 \text{ cm}^2/\text{g}$ using BET studies. The rGO helped to increase the surface area of vanadium oxides which will improve the electrocatalytic activity of the composite cathode material. Even after 100 cycles, the discharge specific capacity of V_2O_5 /rGO was 171 mAh/g , which is 1.3 times greater than pure V_2O_5 implying the higher electrocatalytic activity of rGO. In addition to specific capacity, the addition of rGO to V_2O_5 also improved the cyclic stability of the nanocomposite. Hence, V_2O_5 /rGO was found to be a potential candidate as carbon composite for Li-ion battery application [38].

Linfei Zhang et al. reported V_2O_5 -C- SnO_2 synthesized using hydrothermal method as anodes for Li-ion batteries. In this work, glucose is used as carbonating agent and V_2O_5 and SnO_2 are linked to carbon to achieve high power and energy density. The nanocomposite retained reversible capacity of 800 mAh/g after 100 cycles which proved the cyclic stability of the synthesized nanocomposite material. The resistance was calculated from electrochemical impedance spectroscopy which showed lower resistance for the V_2O_5 -C- SnO_2 than V_2O_5 / SnO_2 . The work showed

that the carbon addition to V_2O_5/SnO_2 improved its reverse cyclic stability and rate capability suitable for Li-ion battery application [35].

4.4 Carbon Dioxide (CO_2) Reduction

Two major challenges prevailing in this century is global climate change and energy demand. To enjoy a sustainable environment both these challenges must be met using renewable energy sources. Carbon dioxide (CO_2) one of the major greenhouse gas responsible for climate change must be controlled or converted to any useful gas/or fuels. In that row, the research is carried out widely to covert CO_2 to fuels even before its release into the environment. The electrocatalyst plays a major role in electrochemical reduction of CO_2 and several reports indicate that carbon based electrocatalyst are efficient electrocatalyst for the CO_2 reduction. Xing Zhi et al. reported the interfacial electron transfer characteristics of graphitic carbon nitride (g- C_3N_4)/graphene doped with heteroatom boron, nitrogen, oxygen and phosphorous towards CO_2 reduction reaction through density functional theory (DFT) computational analysis. The work suggested that the carbon atom (C1) in the g- C_3N_4 , acts as an active site and the graphene provides better conductivity in the reaction. Increase in electron transfer was observed when nitrogen is doped with graphene. The strong adsorption capacity of g- C_3N_4 towards CO_2 makes it an ideal material for CO_2 reduction reaction [2].

Xunyu Lu et al., reported the CO_2 reduction of covalently bonded g- C_3N_4 /multiwall carbon nanotube nanocomposite. The bonding between carbon and nitrogen of multiwall carbon nanotube and g- C_3N_4 acted as core active sites for CO_2 reduction reaction. The highlights of g- C_3N_4 /multiwall carbon nanotube nanocomposite is its conductivity, active sites due to C-N bonding, increased specific surface area and mainly the aggregation of g- C_3N_4 could be hampered through multiwall carbon nanotube addition which results in higher surface area improving the catalytic performance for better CO_2 reduction reaction [8].

M. Nur Hossain et al. reported copper/reduced graphene oxide (Cu/rGO) nanocomposite for CO_2 reduction. The work also studied the Faradaic efficiency of the Cu/rGO catalyst using chemical oxygen demand for the first time. The chemical oxygen demand method which is different from CO_2 reduction, measures the total number of electrons taken part in the conversion of CO_2 gas to any other gas or fuel. While coming to the electrochemical characteristic study, linear sweep voltammetry and chronoamperometry are majorly used to understand the electrochemical behaviour of Cu/rGO nanocomposite. From the study it was found that the Cu/rGO nanocomposite exhibited minimum onset potential and better energy density compared to pure Cu nanoparticles as well as pure rGO implying that the synergistic effect of Cu/rGO nanocomposite plays a tremendous role in influencing the catalytic activity. From electrochemical impedance spectroscopy, the charge transfer resistance of Cu/rGO nanocomposite was found to be 355.40 Ω/cm , whereas R_{CT} value of pure Cu nanoparticles was 612.90 Ω/cm . In addition to R_{CT} value, the constant phase element value of Cu/rGO nanocomposite (1817.60 $\mu F/cm$) was also higher

than pure Cu nanoparticles (427.38 $\mu\text{F}/\text{cm}$) and rGO (781.40 $\mu\text{F}/\text{cm}$). For better electrochemical performance, the electrocatalyst must possess lower R_{CT} value and higher constant phase element value and hence the values observed in this work proves that Cu/rGO nanocomposite is an efficient electrocatalyst. In the cathodic potential range -0.4 to -0.6 V, it was found that carbon monoxide (CO) production from CO_2 was increased. This work confirmed that Cu/rGO nanocomposite exhibited higher Faradaic efficiency and lower overpotential making Cu/rGo a better candidate for CO_2 reduction [39].

5 Summary and Future Perspectives

The research on efficient electrocatalyst is thriving among researchers worldwide due to the demand for sustainable energy devices. The existing efficient electrocatalyst that are into commercialization are majorly noble metals (Pt, Ru, Ir) which are expensive and less abundant. In order to overcome these limitations of the existing electrodes, carbon-based materials are explored at a larger scale. The carbon-based nanocomposites with heteroatom doping, introducing functional groups, developing composites with metal oxides and sulphides are found to be effective. Though carbon-based materials are making a revolution in developing renewable energy devices, understanding the mechanisms underlying the improved electrocatalytic activity while making carbon integrated composites needs further exploration.

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