

# TMCs, TMNs as LOB catalyst

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A large volume of research on lithium–oxygen (Li–O<sub>2</sub>) batteries (LOBs) has been conducted in the recent decades, inspired by their high energy density and power density. However, these future generation energy-storage devices are still subject to technical limitations, including a squat round-trip efficiency and a deprived rate-capability, due to the slow-moving electrochemical kinetics of both the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) over the surface of the cathode catalyst. Because the electrochemistry of LOBs is rather complex, only a limited range of cathode catalysts has been employed in the past. To understand the catalytic mechanisms involved and improve overall cell performance, the development of new cathode electrocatalysts with enhanced round-trip efficiency is extremely important. In this context, transition metal carbides and nitrides (TMCs and TMNs, respectively) have been explored as potential catalysts to overcome the slow kinetics of electrochemical reactions.

Keywords: Li–O<sub>2</sub> battery ; molybdenum carbide ; titanium carbide ; nitrides ; OER/ORR ; Li<sub>2</sub>O<sub>2</sub>

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## 1. Introduction

The environmental pollution and climate change caused by the use of fossil fuels have been major causes of concern worldwide. To restrict the consumption of fossil fuels, alternative renewable energy storage devices with an enhanced energy density and power densities, including lithium-ion batteries (LIBs) <sup>[1][2][3][4]</sup>, lithium-air (Li–O<sub>2</sub>) batteries (LOBs) <sup>[5][6]</sup>, and supercapacitors (SCs) <sup>[7][8]</sup>, have been developed for use in applications such as hybrid electric vehicles, off-grid electricity, and miniaturized electronic devices. LIBs and LOBs are also widely employed in high-energy devices due to their longer self-discharging time and excellent specific capacity. The specific energy density of LOBs (a theoretical and practical energy density of 5200 Wh kg<sup>-1</sup> and ~1000 Wh kg<sup>-1</sup>, correspondingly) is larger than that of LIBs (200 Wh kg<sup>-1</sup>) <sup>[9]</sup>, meaning that LOBs are able to power electric vehicles for more than 500 km on a single charge.

However, their poor capacity, large polarization during the charge-discharge process, short lifespan, sudden fade in capacity, and sluggish electrochemical kinetics for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) has restricted commercialization of LOBs, while their storage capacity also needs to be increased for commercialization. In addition, the large-scale production of these batteries needs further research attention because it is not easy to attain high energy and power density simultaneously and because current fabrication processes are expensive and have safety issues. To overcome these drawbacks, nano-carbonaceous materials such as graphene, graphene oxide, carbon nanotubes (CNTs) and, their composites, transition metal chalcogenides, metal-organic frameworks (MOFs), and transition metal carbides (TMCs) and nitrides (TMNs) and their two-dimensional (2D) layered composites (MXenes) have been investigated because of their inherent synergistic physicochemical and electrochemical properties.

In the past two decades, the discovery of graphene and its unique properties has opened up a new avenue of research with regards to 2D materials <sup>[10][11][12][13][14][15]</sup>. Graphene and its composites have thus been broadly utilized in energy storage and conversion devices, but, due to the mono-layer thickness of graphite, they offer only a limited range of applications. On the other hand, graphene analogues, including 2D layered transition metal oxides, phosphides, sulfides, and selenides, have been considered capable candidates for use in energy storage devices because of their ultrathin nature and planar topology <sup>[16]</sup>. However, due to their low working potential, poor specific capacity, weak cyclability, and high-temperature synthesis, these compounds have yet to be commercialized. In the past decade, MOFs and their nanocomposites have also been investigated as excellent candidates for use in LIBs and LOBs owing to their adjustable physicochemical characteristics and ultra-high surface area. Nevertheless, the cycling performance of MOF-based electrodes is inferior to transition metal sulfides and selenides <sup>[17]</sup>.

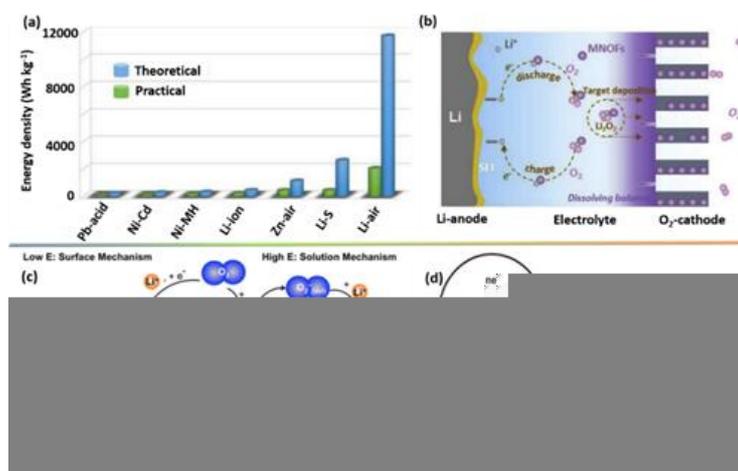
In recent years, numerous efforts have been made to find an alternative to noble metal catalysts and to design non-precious metal catalysts, including 2D transition metal chalcogenides, metal oxides, and metal carbides and nitrides. Of these, TMCs and TMNs have received particular attention due to their outstanding catalytic performance and high electrode material stability, which is similar to that exhibited by commercial Pt-C catalysts. In addition, their 2D layered form MXene and its composites have been employed in various materials science applications, including energy storage devices. As shown in Figure 1, TMC/TMNs including MXenes offer high electrical conductivity, hydrophobicity, the quick diffusion of ions and molecules, easily adjustable structures, good thermal stability, a tunable structure and thickness, and a high surface area [18][19].

**Figure 1.** Schematic illustration of the properties of transition metal carbides (TMC)/ transition metal nitrides (TMN) including MXenes.

To date, a handful of reviews have been published on energy storage and conversion applications involving metal carbide and nitride-based nanostructured electrodes [20][21]. In particular, a number of reviews have summarized the synthetic strategies for and the role of MXenes in energy storage and conversion based on studies published before 2017 [22][23][24][25]. Very recently, Jun et al. provided a complete overview of MXene compounds for environmental and electrochemical storage applications [26], while the mechanisms of delamination and the role of MXene electrodes in dictating the cycling properties of LIBs were examined thoroughly by Zhang et al. [27]. However, these studies have not addressed the evolution of TMCs/TMNs into 2D layered TMCs/TMNs (i.e., MXene-based compounds) in the context of LOBs, and the electrochemical performance and storage properties of these batteries have not been summarized in detail. Therefore, a review that specifically focuses on nanostructured TMC/TMN cathode catalysts for LOBs has been long overdue. Because the role of anodes and electrolytes in LOBs have been extensively reported elsewhere [28][29], we do not address these in the present review; rather, we provide a comprehensive review of the electrochemical, physicochemical, and storage properties of both bulk and 2D layered TMCs and TMNs, counting the carbides and nitrides of Ti, V, Fe, and Mo and their composite counterparts, when used as active cathode catalysts in rechargeable LOBs.

## 2. Basic Principles of Li–O<sub>2</sub> Batteries

LOBs represent a rechargeable energy storage technology that has received significant research attention as a way to meet future energy demands. In theory, LOBs have a higher energy density than gasoline and other storage devices [30] (Figure 2a), thus, they are expected to replace gasoline for use in road, aquatic, and aerial vehicles [31][32][33][34][35][36][37][38][39][40].



**Figure 2.** (a) Theoretical and practical energy density of various energy storage devices [30]. Copyright 2020 Elsevier. (b) Graphic illustration of different components of an Li–O<sub>2</sub> battery (LOB) [6]. Copyright 2020 Elsevier. (c) Expected oxygen reduction reaction (ORR) mechanisms in an LOB [39]. Copyright 2016 The American Chemical Society. (d) Expected oxygen evolution reaction (OER) mechanisms in an LOB [40]. Copyright 2013 The American Chemical Society.

Littauer et al. first described the interesting Li–O<sub>2</sub> chemistry in 1976 [35], after which Abraham et al. demonstrated the LOB system using a non-aqueous electrolyte in 1996 [36]. As shown in Figure 2b, a typical LOB system consists of a negative electrode (Li metal), a positive electrode (primarily a carbonaceous material), and an electrolyte (generally divided into aqueous, non-aqueous, hybrid, and solid electrolytes). During the electrochemical reaction in LOBs, Li<sub>2</sub>O<sub>2</sub> is formed as a by-product of the interaction between O<sub>2</sub> and Li<sup>+</sup> during the discharge process before decomposing again during subsequent charging.

Because the positive electrode (i.e., cathode) provides a reaction site for the electrochemically active  $O_2$  and  $Li^+$  and stores  $Li_2O_2$ , it plays pivotal role in the storage capability of LOBs and the reversibility of Li-ions [37][38]. A significant volume of research activity has thus been devoted to the optimization of cathode electrodes in LOBs. The specific surface area, electrical conductivity, pore size, and volume of the cathode active material are considered the most influential properties for enhancing the storage capability and reversibility of LOBs. The electrochemistry of cathode electrodes needs to be well-understood in order to identify optimum active cathode materials for use in LOBs. At the cathode electrode,  $Li_2O_2$  is formed via the ORR in two steps: (1)  $O_2$  binds with unoccupied O-positions to produce  $O_2^-$  (superoxide) and (2)  $O_2^-$  reacts with Li through the dismutase process to produce  $Li_2O_2$ . A schematic illustration of the ORR in a LOB is presented in Figure 2c [39]. Because the decomposition voltage of  $Li_2O_2$  is much higher (3.75 V vs.  $Li/Li^+$ ) than the plateau potential of 3.4 V, it is unstable. As illustrated in Figure 2d, the decomposition of  $Li_2O_2$  occurs via the OER in another two-step process [40]: (1)  $Li_2O_2$  releases one electron and decomposes to  $LiO_2$  and (2)  $LiO_2$  interacts with oxygen vacancies to release the second electron and lithium ions. As a result, LOB operation completely relies on the OER and ORR during the electrochemical charge–discharge process [41][42][43].

## 2.1. Basic Requirements for an Air Cathode

The chemical and physical properties of  $Li_2O_2$  determines the capacity, cycle overpotential, rate capability, and cycle life. Cathode electrodes in LOBs are thus designed in consideration of the physical and chemical properties of  $Li_2O_2$ . In general, the choice of an air electrode for a rechargeable LOB depends on maximizing its  $Li_2O_2$  ability with stronger ORR and OER electrocatalytic behavior. In particular, stable air cathodes should have the following properties to achieve better LOB performance:

- High electrochemical and chemical stability are necessary to reduce the overpotential during charging, which results in a reversible electrochemical reaction at satisfactory charge–discharge potentials, with less chance of irreversible sponging reactions.
- A high specific surface area with a mesoporous structure enhances the discharge capacity even at high current densities, which is an important criterion for the high storage of  $Li_2O_2$ .
- To increase the rechargeability, a large packed electrode with a lower void volume is essential because it can prevent electrolyte penetration and improve the electrochemical reaction at catalytic sites due to the enhanced transportation of active  $O_2$  and  $Li^+$ . Therefore, an electrode with a porosity that is appropriate for the size of  $Li_2O_2$  exhibits greater rechargeability.
- Electrical conductivity is a deciding factor for renewable energy storage performance; hence, a cathode with greater electrical conductivity is required to allow the consistent transportation of electrons from the insulator and  $Li_2O_2$  to the surface of the cathode.

Based on these considerations, various nanostructured carbonaceous materials have been investigated as active cathode materials in LOBs [44][45]. Carbonaceous materials are predominantly used as a cathode in LOBs due to their high specific surface area for the formation of  $Li_2O_2$ . To enhance the properties of these carbon materials, their morphology can be changed into CNTs and carbon nanofibers (CNFs). The one-dimensional (1D) architecture of CNTs and CNFs enhances the efficiency of charge transfer and the dimensional stability of the electrode during the charge–discharge process and its cycle life [46][47]. Despite their advantages, CNTs and CNFs have issues with the agglomeration of particles during the electrochemical process, which weakens the performance of LOBs. To overcome this, 2D graphene was introduced as potential cathode active material for LOBs, though the re-stacking of graphene sheets as the number of cycles increases has become a concern [48][49][50]. To avoid this re-stacking, various metals, metal oxides, and heteroatoms have been introduced into the graphene architecture [51][52][53]. The synthesis of three-dimensionally (3D) ordered mesoporous carbon and MOFs have been introduced to avoid the self-aggregation of carbon particles [54]. Not only does the aggregation of carbon particles cause concern, the formation of  $Li_2CO_3$  during the charge–discharge process is also a problem. The emergence of an insulating layer  $Li_2CO_3$  on the exterior layer of the carbon electrode increases the interfacial potential, resulting in higher charging potentials and a lower round-trip efficiency for LOBs [55][56].

Recently, carbon-based cathode electrodes have been replaced with other materials based on metals, metal oxides, carbides, nitrides, sulfides, and their composites to prevent the formation of  $Li_2CO_3$  as a by-product. After extensive research, nanoporous gold and platinum have been identified as the most promising metals for the decomposition of  $Li_2O_2$  at a low potential, but the cost of electrode fabrication is a major concern [57]. In terms of oxide-based materials,  $V_2O_5$  [58],  $Co_3O_4$  [59],  $Al_2O_3$  [60], and  $MnO_2$  [61] have generated significant interest, but these materials induce a significant increase in potential that acts as a hurdle for the transfer of electrons. Currently, carbide- and nitride-based cathode electrodes are under investigation as materials for energy storage devices [62][63].

## 2.2. Characterization Techniques for TMCs and TMNs Cathode Catalysts

As we mentioned above, the present review is primarily focused on the cathode catalysts for LOB applications. Some of the significant physicochemical and electrochemical characterization techniques for TMCs and TMNs are discussed in this section.

### 2.2.1. Physicochemical Characterization Techniques

In general, the anode or cathode materials are characterized physicochemically through various types of spectroscopy and microscopy techniques such as field emission-scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses. The microscopic analyses using FE-SEM and HR-TEM are used to probe the morphological evolution of electrode materials during the galvanostatic charge-discharge (GCD) process, which affords a vision into the favored reaction sites. The damage caused by the electron-beam of FE-SEM analysis is almost less than that caused by HR-TEM, which makes it feasible to analyze the reaction products and by-products such as  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$ , respectively, which are highly unstable when exposed to an electron beam [64][65]. In order to avoid such risk factors, in-situ HR-TEM has employed to study the electrochemical process of  $\text{Li-O}_2$ , which provides temporal and spatial resolution and does not mimic the cell's environment as much as compared to other microscopic analyses. XRD study is used to determine and quantify the crystallinity of the reaction product/by-product include  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$ . Furthermore, the electrochemical oxidation of the reaction site products can be monitored by in-situ operando-XRD analysis during GCD process. Another important technique of XPS has been used to evaluate the surface chemistry and spatial distribution of GCD reaction products, including  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$ , and also provides the basic knowledge on these reaction products interactions with the electrolyte and electrodes. The BET analysis provides the complete understanding of porosity properties of the cathode catalysts such as pore volume, surface, and diameter and plays a key role to evaluate the discharge capacity of the LOB cell.

### 2.2.2. Electrochemical Characterizations

Usually, the cathode catalysts for electrochemical tests are prepared in a standard procedure as described earlier [66]. In brief, the as-prepared TMCs/TMNs cathodes (loading mass = 1–3 mg) are mixed together with binders (Kynar<sup>®</sup> HSV 900 and Kynar<sup>®</sup> HSV 1810) and super carbon in a stoichiometric ratio of 3:1:1 or 4:1:1 in N-methyl-N'-pyrrolidone solvent to form a slurry. The attained slurry was coated over a substrate by doctor blade method. The thickness of the coating material is maintained around 90–100  $\mu\text{m}$ . The coated substrates were dried under vacuum at 80–100  $^\circ\text{C}$  for about 12 h and then laminated into disks. The binder-free cathodes have also been studied and reported elsewhere owing to the binder's decomposition with ether-electrolytes during the cycling process. The LOB assembly could be achieved in the following manner: a Swagelok cell consists of a piece of lithium foil over a stainless steel at the anode end and clean  $\text{O}_2$  is applied on as-prepared catalyst at the cathode end. The electrolyte either protic or aprotic immersed Celgard/glass fiber separator is placed in between them; then, the whole cell set-up is sealed in a glass container that is filled with clean  $\text{O}_2$ . Considering the sensitivity of LOBs, the whole experiment should be done under inert atmosphere. The prepared Swagelok cells can be subjected into multiple electrochemical characterization analyses such as cyclic voltammetry (CV), electrochemical impedance analysis (EIS), and galvanostatic charge-discharge (GCD) analyses. To identify the electrocatalytic mechanism and performance of LOB, CV, and GCD, analyses need to be performed at different scan rates and current rates, respectively. However, the formation of by-products such as  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$  during cycling process are unavoidable due to the side reactions, which include electrolyte and binder decomposition at the electrode and electrolyte interfaces. Nevertheless, the side reactions and formation of by-products can be largely controlled nowadays by the rational design of electrode materials and various synthesis strategies.

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