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Transition Metal Oxides as Electrocatalytic Material in Fuel Cells: A Review

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Abstract

Fuel cells make use of electrochemical reactions to produce electricity and majority of the devices have almost no carbon emissions. These devises, and other environmentally friendly energy systems alike, have gained more and more popularity and necessity in the face of high levels of hazardous pollutants accumulated over the years. Electrocatalysts form part of the components of the membrane electrode assembly (MEA) and are a key part in the fuel cell systems. Furthermore, electrocatalysts play a crucial role in supporting electrodes to promote various electrochemical reactions needed to generate energy. Nanostructured transition metal oxides (TMOs) are among the most suitable material candidates for these applications. The interest in TMOs is not new; nanostructured compounds of these materials have good catalytic activity, good durability and high efficiency and have been an interest in catalyst research for years. Studies and developments have reported impressive progress towards these catalyst materials as promising candidates to promote the mass commercialization of fuel cells. Up to now, platinum and platinum group metals have been the ideal choice due to their outstanding properties, however researchers have had to explore other TMs which do not have the let-down of lack of abundance and high cost. Many reviews have been done on the strides made on the invention and developments made over the decades and TMs are no exception to the list. However, platinum, titanium, tungsten, tin and iridium have received more attention and very few papers have been published on the overall oxides of TMs. With the aim of bringing understanding to why TMs contribute greatly towards the improvement studies of catalytic performance, this review discusses recent published studies on progress made to develop TM oxides as electrocatalytic materials in varied applications of fuel cells.

Keywords: Transition metals; Nanostructured oxides; Electrocatalysts; Fuel cells.
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1. Introduction

Transition metal oxides are adopted in fuel cells applications as electrocatalyst due to their abilities in charge transfer with adsorbed molecules.[1] Generally, transition metal oxides exhibit good catalytic activity in the oxidation reduction reaction (ORR). Their availability ranges from rare and expensive; considering the platinum group metals to plenty other abundant and cost friendly materials from the 'd' block[2] providing a wide selection during material design. For these reasons, transition metal oxides (TMOs) have increasingly gained interest in industrial applications and in catalysis studies,[3] more so in the research and development of fuel cell technology. Fuel cells are a clean, sustainable and renewable technology that provides a solution to generating energy from fossil fuels which have devastating impacts to the environment and ultimately the human life. The global urgency to switch to environmentally cleaner solutions has open up a commercial need for conversion technologies such as fuel cells.[4]

Different types of fuel cells have been designed and developed since their first invention in the 1800s; however, they all subscribe to the same working principle and are assembled similarly. They convert electrochemical energy to electrical energy with littles to no harmful emission.[5] In fuel cells, there are three primary segments in each design, namely, an anode, cathode and an electrolyte between the two.[6] The type of a fuel cell is determined by the electrolyte, liquid or solid.[7] The polymer electrolyte membrane is one of the most studied types of cells. A typical representation of a fuel cell is presented in Fig. 1. Fuel cells are reliable, sustainable and offer longevity in back up power systems,[8,9] in marine applications[10] and in transportation and residential applications.[11] Honda, Toyota and Hyundai have made stride in the mass production of vehicles running on hydrogen fuel cells.[12,13] Fuel cell based transportation, power plants, and

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electricity generators can be expected to become prominent in the coming decades.[14]

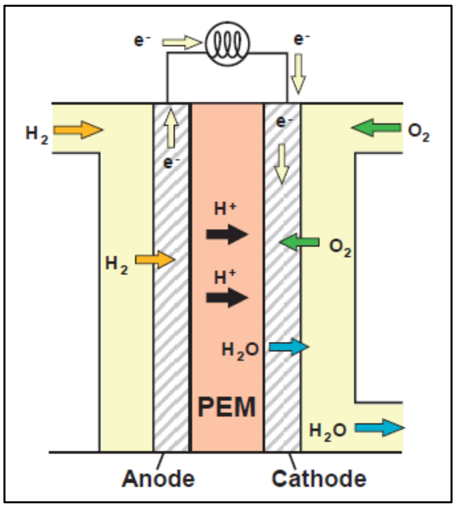

Fig. 1 Schematic Representation of a PEMFC. Reproduced with the permission from [15].

At the core of fuel cell systems lies the membrane electrode assembly (MEA), which require outmost tendering during synthesis.[16] The membrane is made up of the anode, cathode, catalyst and gas diffusion layers. The layers are responsible for different functions such as the transfer of reactant/ product species, charges, and heat.[17] At the anode, a hydrogen-containing fuel is fed, and a catalyst layer is placed to split the fuel into electrons and protons. Protons travel through the electrolyte, which only permits positively charged ions to move through while an alternative and path is provided for the electrons to travel to the cathodic side of the cell. Oxygen, usually from air, is fed at the cathode. There, the oxygen reacts with both the hydrogen protons and electrons to form water which then leaves the systems. The movement of the electrons from the anode to the cathode is collected as electricity.[18] Fuel cells can operate at low and high temperatures. Noble metal catalysts such as platinum, are usually chosen for low temperature applications. Hydrogen rich fuels, such as hydrocarbons and alcohols together with an oxidant can be adopted for energy production in fuel cells however hydrogen is mostly used and considered to show higher electrochemical reactivity. When other fuels are used, they are broken down into hydrogen and other elements thereafter the electrochemical process proceeds. The abundance of air provides oxygen as a highly reactive oxidant.[19] Despite their excellent properties, transition metal oxides are limited by poor conductivity, low energy density and sluggish electrochemical kinetics.[20] Other than the cost barrier, platinum is commonly used as the catalysts later due to its excellent properties. Due to its cost, platinum loading is preferred to be low without compromising the activity, durability and stability of the materials.[21] This is done by adding support to the platinum to increase the surface area. The catalyst and support materials chosen are usually porous structures and they are responsible for promoting the cell reactions. During operation, the materials can be prone to degradation, for this reason material selection should consider chemical and electrochemical stability.[22] A schematic representation of the degradation of MEA undergoing dissolution, agglomeration and detachment of catalytic nanoparticles is presented in Fig. 2.

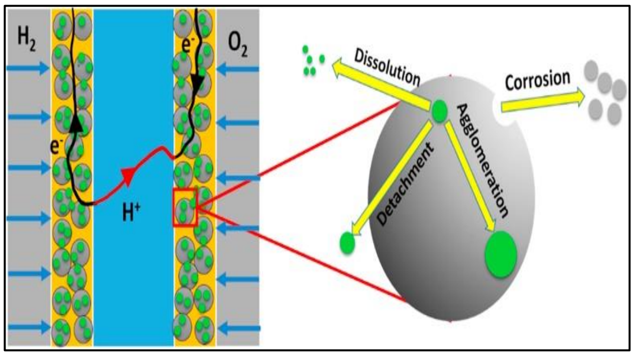

Fig. 2 Schematic illustration of MEA and the degradation of electrocatalysts. Reproduced with the permission from [22], Copyright 2016 Elsevier Ltd.

To date, numerous reviews have been done on a handful metals of the TMs group; graphene, carbon nanotubes, mesoporous carbon, and doped carbon nanostructures, some metals oxides borides, nitrides, carbides and hybrid nanocomposites. Among the transition metal oxides, titanium, tungsten, tin and iridium oxides have received the most attention. In this paper, we seek to summaries recent developments on all the oxides of TMOs in different applications; the ongoing progress in overcoming the limitations from sluggish electrochemical kinetics and expensive costs of using PG metals.

2. Fuel cell reactions

The fuel cell makes use of a reduction oxidation reaction to generate electricity just as observed in a typical galvanic reaction. The fuel fed into the anode is split into 2 positively charged ions and 2 electrons through oxidation. The positively charged ions then travel through the electrolyte, however, the electrons cannot pass through an electrolyte with its negative charges, therefore, and an external alternative path is created through a conducting wire for the electrons to move to the cathode. Finally, the air fed into the cathode reacts with the positively charged ions and electrons and the output is usually water.[23] The movement of electrons through the conducting wire generates electricity or load which is used to power devices.

The electrochemical reactions that take place inside of the fuel cell are a reversal of the water splitting process, also known as electrolysis. The quality of the gases fed into the fuel cell systems along with the catalytic properties of the materials in the membrane influence the voltage output.[24] Two half-cell reactions inside the fuel cell; the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR).[25] The HOR takes place at the anode as described in Eq. (1):

$$H_2 \rightarrow 2H^+ + 2e^- \qquad E^0 = 1.229\ V \tag{1}$$

HOR has faster kinetics to ORR, even at low Pt loading the reaction is enabled. For this reason, HOR tends to receive less attention. However due to the low Pt loading, the HOR overpotential is not necessarily negligible.[26] The oxidation reduction reaction (ORR) is a multi-electron reaction six or more orders of magnitude slower kinetics than the HOR.[27] The outputs of this reaction depend on the medium; in acidic medium, a four-electron process yields water, whereas in alkaline medium, a four-electron and two-electron process yields hydroxides. ORR in acidic medium can be described in Eqs. (2-4) as follows:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.229\ V \tag{2}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0 = -0.695\ V \tag{3}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^0 = 1.776\ V \tag{4}$$

ORR in alkaline medium can be described in Eqs. (5-7) as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^0 = 0.401 V \tag{5}$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad E^0 = -0.076\ V \tag{6}$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad E^0 = 0.878\ V \tag{7}$$

Most of these electrochemical reactions occurring in fuel cells can be broken down into a series of steps, which include mass transport, adsorption, dissociation, electron transport and mass transport.[28]

3. Properties of TMOs

For transitions metals, atoms of oxygen form oxides with the metals easily due to their partially filled outer orbitals. Numerous compounds of TM oxides are already in existence and a large fraction of these assume a solid crystalline form at set environmental circumstances.[29,30] The design of a catalyst is also gravely affected by the relationship between the structure and reactivity of its oxide surfaces.[31] The structural arrangement of the metal cation and oxygen anion influences the relative acidity and basicity of the atoms present on the surface of metal oxides, which alter the catalytic properties of these compounds.[32] Evidently, the outer subshells of TMs are responsible for the wide scale of properties that range from oxides with metallic properties (mainly electronic and magnetic) to highly insulating properties. In Table 1, the oxidization states of transition metals are presented. The altering of operational conditions during synthesis such as the composition of the material, temperature and pressure allows for the manipulation of the desired final attributes.[33] The chemical attributes of TMs stretch wide, from metals that are strong reducing agents to those of very low reactivity. Precious metals have a high resistance to oxidation, causing them to exhibit high reduction potentials.[35] The electrochemical potential of transition metal catalysts goes higher along with the number of electrons in d orbitals of transition metal elements of the same period.[36] This is illustrated in Fig. 3.

The particle size and catalytic activity is a key relationship to the electrocatalysis of oxygen. Studies have shown that because nanoclusters of transition metal oxides have a larger surface-to-volume ratio to that of nanoparticles, they are able

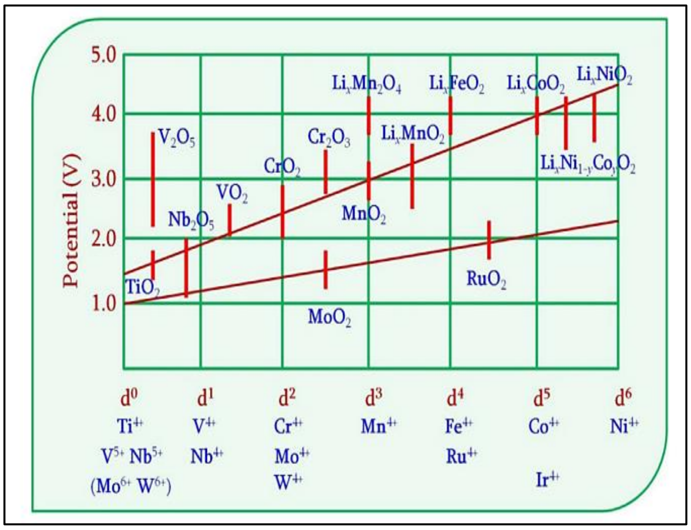

Fig. 3 Schematic illustration of the electrode potential and the number of electrons in the d orbitals interaction of transition metal ions. Reproduced with the permission from [36], Copyright 2015 The Authors.

Table 1. Oxidation states of the transition elements.[34]

Element	Oxidation state							Element	Oxidation state								
Scandium			3					Technetium			2		4	5			
Titanium		2	3	4				Ruthenium			2	3	4	5	6	7	8
Vanadium		2	3	4	5			Rhodium			2	3	4		6		
Chromium		2	3	4	5	6		Palladium			2	3	4				
Manganese		2	3	4	5	6	7	Silver		1	2	3					
Iron		2	3	4	5	6		Cadmium			2						
Cobalt		2	3	4	5			Hafnium				3	4				
Nickel		2	3	4				Tantalum			2	3	4	5			
Copper	1	2	3					Tungsten			2	3	4	5	6		
Zinc		2						Rhenium	-1	+1	2	3	4	5	6	7	
Yttrium			3					Osmium			2	3	4		6		8
Zirconium			3	4				Iridium			2	3	4		6		
Niobium		2	3	4	5			Platinum			2	3	4	5	6		
Molybdenum		2	3	4	5	6		Gold		1		3					

to provide more active site to promote electrocatalytic reactions.[37] In fuel cell applications, catalyst are required to be and porous and have a large surface area to enable more reaction sites, the catalysts must be corrosion resistant andhave strong metal–support interaction, and stable structure.[38] According to *Us et al*. “The Sabatier principle states that the highest reaction rate occurs when the adsorption of reaction species on the catalytic sites is neither too strong nor too weak. This leads to the construction of a volcano-shaped structure−activity relationship when plotting the reaction rate against descriptors such as the adsorption energy of intermediates. The volcano summit has, therefore, been regarded as the optimal region for the best performance”. The ORR volcano plot for transition metal catalysts is presented in Fig. 4. The electron interaction has a large impact of the crystal structure and stoichiometry of transition metal oxides. Therefore, beyond the volcano summit, the design of TMO-based electrocatalysts also takes into consideration the spin, charge, and orbital states. The multiple crystal structures and compositions of TMO have enabled the modifications for improved catalytic activity. The d-orbitals, which is partially filled for the majority of the TMO is responsible the form the electronic structures of TMOs will take.[39]

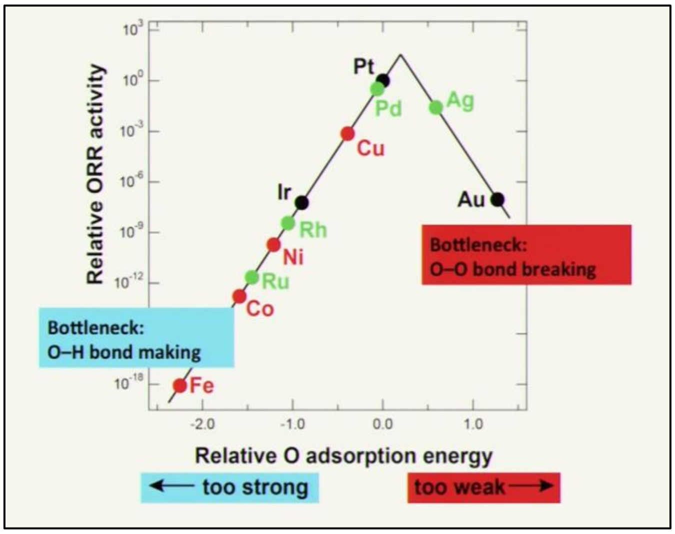

Fig. 4 ORR volcano plots for transition metal catalysts.

4. Transition metal oxide-based electrocatalysts

4.1 First transition metal series

After calcium, the elements on the periodic table exhibit a significant shift of properties. From scandium through to copper which make up the first transition series, the elements begin to show similar physical and chemical properties due to relatively small effective nuclear charge. Literature describes that “each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell”. Oxidation states of scandium, titanium, and vanadium typically show the most stability, however, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series.[35] With the current obstacle in the commercialization of electrocatalysts being rarity and cost, titanium, vanadium, chromium, manganese and iron have the advantage of being part of the most abundant metals on the Earth’s crust. By definition, a TM is a stable ionic element whose d shell is incompletely filled. The 3d shell for all compounds of scandium have no electrons occupying them while those of zinc are completely occupied.[40]

4.1.1 Scandium, Titanium and Vanadium

Oxide composites of scandium are not electrically conductive except for some perovskite structures which are adopted for cathode applications in solid oxide fuel cells. The metal is also a doping agent for the enhancement of other metals.[41] Recent publications have few to not work done on scandium and scandium oxide-based materials as cathode catalyst of fuel cells.[42,43]

In catalytic applications, nanoscale titanium oxides are adopted as supporting materials, usually in combination with other metallic elements.[44] Hornberger *et al.* adopted ruthenium-titanium mixed oxide (RTO) supports for the oxygen reduction reaction of platinum nanoparticles and reported remarkable structural stability towards dissolution. Nevertheless, the catalytic activity seemed to decrease over time, jeopardizing the overall ORR activity and CO oxidation. the authors owed this to the possible passivation onto platinum by oxygen due to strong metal-support interaction.[45] Titanium oxide supports have also been reported to outperform carbon supports on the electrocatalytic activity of precious metal nanoparticles. However, Reducing the particle size proved to compromise the catalytic activity.[46] The development of titanium oxide based supporting materials has continued to be popular and recent research findings reveal that titanium oxide composites have remarkable efficiency for this role.[47,48]

Vanadium has a wide range of oxides which possess various crystal structures and chemical properties. Prasadam *et al.* described vanadium oxides VO_2, V_6O_{13}, V_4O_9, V_3O_7 and V_2O_5, as efficient candidates’ materials for electrode applications.[49] For decades, applications of catalysis have benefited from the use of vanadium oxide composites commonly in the form of precursors.[50] Ayyaru *et al.* recently presented vanadium pentoxide (V_2O_5) as a novel cathode catalyst material in air-cathode single chamber microbial fuel cells (SCMFCs). The study found that the V_2O_5 cathode catalyst constructed with the double loading MFC outperformed those constructed with single and triple loading MFC and its that it could function just as efficient as the commercial platinum catalyst.[51]

4.1.2 Chromium, Manganese and Iron

Oxides of chromium compounds are not electrically conductive. However, much like scandium, some perovskite structures of chromium oxides are adopted for cathode applications in solid oxide fuel cells. Chromium oxides are commonly used as catalysts for dehydrogenation of ethane in fixed beds, are applied as anodes in fuel cell reactors.[52] Their high stability makes them suitable for electrochemical application in fuel cells. Literature reports that the presence of chromium with carbonaceous material can enhance the efficiency and durability of the prepared catalyst. Kamya *et al.* recently adopted chromium oxide/nanoporous carbon composite (Cr_2O_3/NPC) as support for platinum/thin oxide nanoparticles for ethanol oxidation reaction and concluded that metal/metal oxide binary composition of catalysts through co-action and synergistic effects increases catalytic activity.[53] The main advantage of utilizing manganese oxide compounds is that manganese has low cost, is abundant in nature, eco friendliness and has good electrochemical properties. Oxides catalysts of manganese exhibit good durability, flexibility and low toxicity which make them a popular material of study in the research communities. Due to these attributes, oxides of manages are adopted in but not limited to microbial fuel cell air cathodes,[54] metal-air batteries and alkaline fuel cells.[55] Studying the comparison between the Low cost α-MnO_2 nanowires and α-MnO_2 nanowires supported on carbon Vulcan (α-MnO_2/C) shows that the presence of carbon support enhances the efficiency of MFCs because of surface structure and higher surface area. The authors report that the stability measurements found are compatible with those of commercial platinum.[56] Similarly, Ding *et al.* reports on the benefits of carbon support.[57] In agreement of carbon support, Shah reports on highly active Mn_xO_y/N-C as a promising candidate to be used as a cathode material.[55] The use of highly efficient but expensive metals along with affordable materials is a common tact. These studies include, Palladium and MnO_2 as cathode catalyst with simultaneous pre-treatment results in higher redox activity of Pd in comparison to MnO_2.[58] Yang *et al.* synergistic interactions of a Co-Mn oxide catalyst which exhibits impressive ORR activity in alkaline fuel cells.[59] Lima *et al.* also describes the effectiveness of the addition of MnO_x on the Pt-MnO_x/C near-surface region. The study found that the nanoparticle science of platinum was not necessarily what contributed to the overall performance of the Pt-MnO_x/C but rather the interaction between the MnO_x and Pt NPs active sites.[60]

Oxides of iron have been a popular choice to microbial fuel cells. Sekar *et al.* reported that Cu-doped FeO nanoparticles coated on anodes of microbial fuel cells presents an affordable choice of materials as well as efficient power density of 161.5mW/m2 necessary for enhancing energy generation.[61] After a 32-day simulated microbial fuel cell test run, two iron-based metal catalysts showed better durability and improved power density 25% more than that of platinum (Pt) and 100% more than activated carbon (AC). Overall, the catalysts proved to be remarkably durable and a far more affordable option for studied for the oxygen reduction reaction (ORR).[62] According to Gorlova *et al.* "the catalytic hydrothermolysis of NH_3BH_3 in the presence of CuFe2O4 is a potentially highly efficient method for hydrogen production for fuel cells at an external heating temperature of 90 °C".[63] Coated on palladium, iron-iron oxide nanoparticles (NPs) increases the current density of palladium 16 times more compared to an untreated palladium catalyst.[64]

4.1.3 Cobalt and Nickel

Studies have also noted that the Substitution of Co^{2+} in the tetrahedral site and Co^{3+} in the octahedral site of Co_3O_4 with inactive Zn^{2+} and $Al^{3+,}$ respectively decreases the ORR in the order of Co_3O_4 (Co_3+ Oh, Co_2+ Th) < $ZnCo_2O_4$ (Co^{3+} Oh) << $CoAl_2O_4$ (Co_2+ Th) in accordance of the ORR overpotentials at the current density of 0.1 mA cm^{-2} Ox. Co^{2+} Oh in CoO is the main active sites, which under electrochemical conditions tends to transform into Co^{3+} Oh and forms Co_3O_4 with hollow structure which remains decent ORR activity.[65]

Ultrafine nanostructured-NiO outperforms the non-modified Ni material. The performance of the metal oxide increases with increase in deposition time during ALD. El-Lateef *et al.* reports that this metal oxide has suitable properties for the remediation of urea-rich wastewater and application in fuel cells and for hydrogen production.[66] To improve the catalytic efficiency of Pd in CO_2 reduction, Fuku *et al.* fabricated NiO as a support. This modification revealed improved current and power densities and high levels of resistance to poisoning.[67] Hierarchical $Ni(OH)_2$–NiS in-plane edge hybrid nanosheets on the carbon cloth surface ($Ni(OH)_2$–NiS-CC) has been reported to exhibit excellent electrocatalytic activity for catalytic electrode applications compared to other Ni based catalysts.[68]

4.1.4 Copper and Zinc

To the best of our knowledge, very littles nanocomposites of copper oxides have been studied recently. Work over the decades however shows that in the electrochemical energy storage and conversion applications, electrodes of granular, single-phase Cu_2O and CuO can be described as extremely active and stable with a capacity retention of about 80% and 85% after 3000 cycles, respectively.[69] TM oxides can also be modified with metals outside the group. The fabrication of Zinc tin oxide (ZTO) thin films with different Sn levels shows that with more Sn contents, the film resistivity gets higher (>1 Ω cm) and the optical bandgap rises from 3.47 to 3.83 eV.[70]

4.2 Second transition metal series

4.2.1 Yttrium and Zirconium

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series.[35] Yttrium Oxides are found in gas sensing technologies,[71] detergents and pharmaceuticals industries.[72] and catalytic applications. A series of Y_2O_3 was prepared to catalyse dimethyl carbonate (DMC) synthesis. The catalyst calcined at 750 °C, showed the best catalytic performance and possessed more moderate acidity and basicity sites, which could efficiently activate CO_2 and CH_3OH.[73] Zirconium Oxide

Doped with Hafnium Oxide by Hydrothermal Method.[74] In clean energy production, electrolytes of scandium-doped zirconia (SDZ) are preferred over those of yttria-stabilized zirconia (YSZ) due to better conductivity.[75]

4.2.2 Niobium and Molybdenum

The niobium oxides are relied on for their capability to act as strong support for other TMs most commonly for modifications for platinum.[76-79] Omidvar agrees that after testing NbO as support for Fe, Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au, the Pt/NbO system shows the most potential for low-cost and high catalytic activity for the oxygen activation reaction.[80] Unless combined with other elements, molybdenum oxide composites for fuel cell applications are not traceable as Mo is not considered to be catalytically active for oxygen reduction reaction (ORR) compared with other transition metals such as Fe and Co.[81]

4.2.3 Technetium, Silver and Cadmium

To the best of our knowledge, no oxides of technetium and silver have been fabricated nor studied for electrocatalytic material in fuel cells. Silver oxide is known to exhibit relatively mild cathode catalytic activity.[82] No oxides of cadmium as fuel cell catalyst materials were traced during this review. Properties of cadmium oxide thin films are rather desirable for semiconducting requirements in applications such as gas sensors, solar and photo-galvanic cells, phototransistors and diodes, transparent electrodes *etc*.[56,83,84]

4.3 Third transition metal series

4.3.1 Hafnium and Tantalum

The physiochemical attributes of hafnium (HfO_2) make it popular for various applications such Nafion-HfO_2 hybrid membranes,[85] catalysts, gas sensors, and fuel cell electrolytes for solid oxide fuel cells.[86] photocatalyst for hydrogen and oxygen production from water[87] among others. In its elemental form, hafnium has a low work function (3.53 eV), high melting point, and acceptable electric and thermal conductivities.[88] Production of hydrogen fuel can therefore be achieved through modification of hafnium as HfO_2 alone has a shortfall of low apparent bandgap energy compared to other hafnium compounds such as $Hf_2O(PO_4)_2$.[87] Another disadvantage of hafnium oxides is that increase in number of deposits hinders the electron transfer through the ceria-based electrolytes in the anode.[89] Other modifications include nitrogen-modified hafnium oxyhydroxide which has been reported to be compatible with the commercial Pt/C as an active and stable electrocatalyst.[90] Studies show that the grain size can be minimized stabilization of the cubic structure can be achieved through doping hafnium with yttrium. From this, characterization revealed a spherical structure from hafnium oxide and a porous lamellar structure from yttrium oxide.[91] Doping of hafnium has seen more interest over untreated hafnium. For this reason, other studies have recently probed into undoped hafnium composites to better understand their morphological characteristics.[92]

Ta_2O_5 thin film can be a promising replacement for Pt as a catalyst in aim of favouring the O_2 reduction reaction in catalytic activity.[93] Utilizing highly dispersed and crystalline Ta_2O_5-modified CNTs as a support to stabilize Pt NPs shows that strengthening metal–support interactions at the atomic scale is an efficient strategy to realize Pt-based electrocatalysts with high durability and activity.[94] Tantalum oxide (Ta_2O_5) layer can also be used a hydrogen sensors.[95] Nanosized Pd particles are loaded onto the Ta_2O_5 surface enhances conductivity and electrocatalytic activity toward ethylene glycol oxidation reaction and are therefore suitable candidates for direct alcohol fuel cell applications.[96]

4.3.2 Tungsten and Gold

Tungsten oxides are one of the most commonly studied composites. Tungsten oxide forms part of affordable materials with good candidacy for electrode catalytic material in Microbial Fuel Cells. While the feasibility of employing PEMFCs in acidic applications has received criticism, WO_3 has received good reviews on the ability to meet both the necessary level of catalytic activity and the affordability aspect.[97] Das and Ghangrekar recently reported five times increment in power production from applying WO_3 on both electrodes of microbial fuel cells. Pitted against the commercialized Pt/C, WO_3 nano-particles have a potential to replace Pt/C.[98] Further alterations to the of WO_3 structure (WO_3/Bi_2WO_6) have reported even better power density and columbic efficiency performance.[99] Aside from replacing platinum based materials, structures of WO_x have been reported to have a noticeable impact on the CO tolerance of Pt/C to overcome poisoning.[100] To the best of our knowledge, no gold oxide composites have been reported in recent years for fuel cell applications.

4.4 Platinum group metals (PGMs)

Platinum group metals, platinum, palladium, rhodium, ruthenium, iridium, and osmium, are known for their high melting points, heat resistance, corrosion resistances, and their unique catalytic properties.[101] Noble metals have a reputation for exceptional catalytic performance, unfortunately due to rarity and therefore cost this has proven to be impractical for mass production in efforts to aid in clean energy transformation. For this reason, precious metals, which exhibit similar behavioural properties to platinum, have been modified in varied ways to attempt the load reduction of the expensive materials.

4.4.1 Platinum, Palladium and Rhodium

Since platinum has been the ideal choice of material for catalyst, it is also relatively the most researched, studied and reviewed element from the transition metal series.[102-104] The majority of the work done is on modifications that enable longer lifespan or reducing the loading of the platinum materials. Adopting a non-TM oxide, Gonçalves et al. adopted

Sb_2O_3 in search of an electrocatalyst and non-enzymatic amperometric sensor for ethanol when modified by Pd nanoparticles. Post modification, morphological evaluations of Pd/Sb_2O_3 revealed change in shape from spherical shape to superficial pores and catalytic activity doubled in comparison with carbon-supported Pd nanoparticles for oxidation of ethanol in alkaline applications [105]. Composites of TM in combination with other materials that are not from the d-block can perform exceptionally well and even though the addition of carbon material have become a popular choice I the past years, non-carbonaceous materials still have a potential to compete.[105] Chung *et al* employed a cheaper material, molybdenum oxide as a modifier for Rhodium and reported exceptional yield rate and a high faradaic efficiency for nitrogen reduction reaction (NRR) applications.[106] The green energy production can also benefit from the fabrication of bimetallic materials. Chung et al. recently proved that Molybdenum oxide decorated on the rhodium (Rh_{MoOx}/C) catalyst can be applied for green ammonia (NH_3) production.[106]

4.4.2 Ruthenium, Iridium and Osmium

The electrocatalytic properties of ruthenium is attractive to a wide range of applications. supported on ruthenium-titanium mixed oxide, the increasing growth of platinum particles does not favour catalytic activity due to poising and agglomeration of platinum of.[45] Iridium oxide compounds are used in anodes of polymer electrolyte membrane fuel cell to help prevent cell reversal.[107] Labi et al. also worked on a study to prevent potential reversal during the operation of a fuel cell. The Pt and IrOx/GV catalyst remained relatively stable when subjected to multiple short periods of fuel starvation. The IrOx/GV MEA was reversal tolerant and provided insight into the degradation processes which occur during periodic and prolonged fuel starvation [108] To the best of our knowledge, oxides of osmium are rather used in other metallic conductivity applications.[109]

4.5 Transition metal oxides on carbon support

A further degree of freedom, which can be used to tune the properties of thin films, is given by the possibility to combine more than one metallic species with oxygen [29] carbon and other materials supports in ternary or multiple oxides. Outstanding electrical conductivity, superior mechanical properties and reliable chemical stability are just a few of the great attributes of TM carbides and the carbon supports are explored in a wide range of forms, and this makes them a popular approach in catalytic supports. Oxide nanoparticles are grown on the surface of carbon nanotube, graphene oxide and graphene,[110] onto glassy carbon electrodes,[111,112] *etc*.

From the early 2000s, when graphene was first discovered, carbon supported electrocatalysts have gained traction. Since then, many TM oxides supported on carbon have been explored for electrocatalysis. Askari et al. also fabricated a catalyst nanocomposite material on reduced graphene oxide (rGO) for a hybrid of $MgCo_2O_4$ in an effort to examine the suitability of $MgCo_2O_4$ as a binary TM oxide (BTMO) for fuel cell anode and MOR process applications. The study deduced that the synergic effect between Mg and Co ions and rGO creates an efficient ternary catalyst with high specific surface area, good conductivity, and excellent stability, which suggests MgCo2O4-rGO as a promising catalyst for the anode electrode of methanol fuel cells.[113] Similarly, Imran et al. made use of reduced graphene oxide (GO) as support for tungsten-molybdenum oxide to enhance strong interface interactions. Plenty more studies have chosen graphene route as a support for enhancement, among them, a new of PVDF-Pt-Pd/rGO-CeO_2 composite nanofibers which is considered a candidate as a novel direct methanol fuel cell (DMFC) catalytic application.[114]

The commercial Pt/C has actually been outperformed by quite a number of new and developed materials over the years. Exploring the use of reduced graphene by modifying the carbon material to nanocomposites of polyaniline (PAni) grafted sulfonated graphene oxide (SGO), Papaya et al. have been able to realize this. Graphene oxide, which is usually relied on as a support on its own is further modified through a diazotization reaction to help promote active sites that heighten the opportunity for ORR. They report on a new transition bimetallic composite (Mn-Co) supported on SGO-PAni as an effective cathode catalyst for the effective generation of bioelectricity. This novel composite is far cost effective and resulted in better power output and power density than Pt/C catalyst.[115] Among all of carbonic morphologies, graphene is the most promising one due to its unique properties. It has a very high surface area, as well as a very high electrical conductivity and improved stability. 3D structured such as Fe-WO_3 nanoflower and reduced graphene oxide and their hybrids are common supports sort after, however, Maiti et al. criticizes that their catalytic performance is not efficient. The authors reported an outstanding catalytic performance, satisfying levels of methanol tolerance and outstanding durability from a three-dimensional (3D) iron tungsten oxide nanoflower anchored nitrogen-doped graphene (3D Fe-WO_3 NF/NG) hybrid and concludes the that the material outperforms Pt/C.[116]

Carbon nanotubes (CNTs) - graphene support is another route. The adoption of multi-walled carbon nanotube (MWCNT) supports has been reported to improve the activity, stability, and resistance of non-supported composites.[117] Sun and Liu fabricated Nano sized manganese oxide flakes on CNTs-graphene surfaces and recorded a far improved ORR activity in comparison to a bland CNTs composite. The study explains that CNTs was found structurally defective and their outer walls suffered cracking into graphene nano pieces during processing, which further enhanced oxygen reductive reaction (ORR).[118]

Other alternative carbon supports include the use of carbon black. Manganese oxides (β-MnO_2/C(N)) supported on carbon black have been proven to have better electrical power density and outstanding cycling stability as opposed to the commercial Pt/C and manganese oxide fabricated on undoped carbon black support (α-MnO_2).[119] After studying iron oxides as part of a carbonaceous complex composite for fuel cell applications, the electrodeposition of three-dimensional nanoflower-like Fe_2O_3 and spherical shaped PdNPs on the g-C_3N_4 nanosheets results in the composite graphitic carbon nitride/iron oxide/palladium nanoparticles (g-C_3N_4/Fe_2O_3/PdNPs). The characterization of the material revealed remarkable durability when compared to commercial Pd/C suitable for direct alcohol fuel cell applications.[120] The use of Iridium oxide catalyst on graphitized vulcan (GV) black (56 wt% Ir) support can also improve the durability of a membrane electrode assembly (MEA).[108]

5. Synthesis of transition metal oxide electrocatalyst

The synthesis of electrocatalytic structures of TM oxides can take multiple routs depending on the desired final properties. Physical and chemical methods are the two primary classes. Chemical methods are further subdivided into gas and liquid phase and include chemical vapour deposition (CVD), plasma enhanced vapour deposition, atomic layer deposition (ALD), spin coating *etc*. physical means of fabrication are subdivided into evaporation and sputtering techniques and include electron beam evaporation, laser beam evaporation, pulsed laser deposition, direct current sputtering (DC sputtering) *etc*.[121-123]

Where high aspect ratio is a requirement for deposition of complex oxide nanostructures atomic layer deposition has proven to be a favourable choice[49] over other synthesis techniques such as chemical vapour deposition (CVD), RF sputtering, pulsed laser deposition (PLD) and molecular beam epitaxy (MBE).[124] This is because ALD allows for a controlled coating with ultralow noble-metal loadings in narrow pores.[125] This nanotechnology synthesis method is popularly sort after for its ability to fabricate ultrathin, uniform, conformal and pinhole-free nano-films.[126] The use of ALD for the fabrication of vanadium oxides for energy storage applications has been highly recommended as it produces electrode materials with outstanding properties.[49] The technology also avails the possibility to adjust the operating parameters to better suit the desired materials output. Hexagonal nanomaterials and cubic CoO structures fabricated through ALD from $CoCl_2$(TMEDA) and water as precursors can be tuned by temperature, water pulse lengths, and type of substrate material.[127] Although transition oxides prepared by ALD as electrodes have delivered remarkable properties for energy storage, Additional surface care may be necessary after ALD processing. Prasadam *et al.* discussed the need for post-deposition treatment of vanadium oxide layers fabricated from ALD to ensure single crystalline phase is achieved.[49] Studies on the development of the technique has afforded clarity on continued ALD growth mechanisms and surface chemistry which eventually be able to contribute to the thin film growth processing.[128]

Cheaper, quick and easy synthesis methods that can be employed include, but are not limited to selective electrochemical etching, which can be performed formed for materials that have a high affinity for oxygen such as chromium and molybdenum[129,130] and spin coating.[131] Similarly, Hernández *et al.* agrees that spin coating is an easy and dependable route for the evaluation of electrocatalytic behaviour of Mn oxide film in pre-synthesized water oxidation catalysts powders.[132] An investigation into the impact of the spin coating speed on physical properties of high quality titanium dioxide–graphene oxide (TiO_2-GO) thin films reported that the deposited films show thinner layers and lower band gap energies with higher spin coating speeds and that an increase in the spin speed leads to a decrease in the transmission level.[133]

6. Summary and outlook

The adoption of metal oxide catalysts and catalysts support from the transition metal series are detailed in this review. Carbonaceous materials, as competing alternatives to transition metal oxides are summarized. Also detailed are some of the commonly utilized synthesis methods for fabricating these electrocatalytic films highlighting the importance of controlling the operating parameters. For instance, doping metal oxide such as zinc and cobalt and carefully controlling the parameters leads to the desired final properties. Transition metal oxides as electrode and catalytic material have held back the mass commercialization of fuel cells due to the devices requiring expensive materials such as platinum, palladium and metals alike. Recent work, however, shows that the inventions and modifications done on electrocatalytic material to overcome costs places the fuel cell technology as a feasible prospect to contribute towards combating carbon emissions. As supports, cost friendly elements such as nickel, cobalt and manganese can reduce the platinum loading and therefore reduce the costs, while also improving the overall activity and stability.

The cost of platinum and platinum group metals have held back the mass commercialization of fuel cells for decades, however with new electrostatic material outperforming Pt/C, the obstacle is now a thing of the past. Inexpensive materials with high resistance to poisoning, activity and stability are a key qualification to replacing platinum and sufficient progress has been made in this regard. Spherical MoO3 fabricated on reduced graphene oxide surpasses the activity and durability of Pt/C and has better tolerance to CO. likewise, graphene (3D Fe-WO3 NF/NG) hybrid shows better methanol tolerance and outstanding durability compared to Pt/C. better electrical power density and cycling stability can also be achieved through the adoption of Manganese oxides supported on carbon black as opposed to Pt/C. In direct alcohol fuel cells, g-C3N4/Fe2O3/PdNPs report more durability when compared to commercial Pd/C. Also impressive is WO3 on both electrodes of microbial fuel cells which is a good candidate to replace Pt/C.

As alternatives to platinum, progress has been made on materials with compatible efficiency. Cobalt molybdenum oxide hydrate grown on nickel foam is comparable to Pt/C use in alkaline medium. Analysis of nitrogen-modified hafnium oxyhydroxide describes the catalyst as just as efficient in activity and stability. Ti0.8Ta0.2O2 composites in alkaline medium have similar activity in comparison to Pd/C catalyst. Carbonaceous supports a better choice to achieving enhancing properties. In a few cases, metal oxide supports can perform better than carbon, titanium oxide supports are a typical example. Catalysts fabricated by oxides of transition metals also outperform their pure state catalyst. For instance, ultrafine nanostructured-NiO performs better the non-modified Ni material. Transition metal oxides have the protentional to challenge the current limitations of fuel cell catalysis.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] M. T. Greiner, L. Chai, M. G. Helander, W.-M. Tang, Z.-H. Lu, Transition metal oxide work functions: the influence of cation oxidation state and oxygen vacancies, *Advanced Functional Materials*, 2012, **22**, 4557-4568, doi: 10.1002/adfm.201200615.

[2] A. Bonnefont, A. S. Ryabova, T. Schott, G. Kéranguéven, S. Y. Istomin, E. V. Antipov, E. R. Savinova, Challenges in the understanding oxygen reduction electrocatalysis on transition metal oxides, *Current Opinion in Electrochemistry*, 2019, **14**, 23-31, doi: 10.1016/j.coelec.2018.09.010.

[3] A. Akbari, M. Amini, A. Tarassoli, B. Eftekhari-Sis, N. Ghasemian, E. Jabbari, Transition metal oxide nanoparticles as efficient catalysts in oxidation reactions, *Nano-Structures & Nano-Objects*, 2018, **14**, 19-48, doi: 10.1016/j.nanoso.2018.01.006.

[4] K.-B. Wang, Q. Xun, Q. Zhang, Recent progress in metal-organic frameworks as active materials for supercapacitors, *EnergyChem*, 2020, **2**, 100025, doi: 10.1016/j.enchem.2019.100025.

[5] R. P. O'Hayre, Fuel cells for electrochemical energy conversion, *EPJ Web of Conferences*, 2017, **148**, 00013, doi: 10.1051/epjconf/201714800013.

[6] S. M. Haile, Fuel cell materials and components, *Acta Materials*, 2003, **51**, 5981-6000, 2003, doi: 10.1016/j.actamat.2003.08.004.

[7] P. Fragiacomo, F. Piraino, M. Genovese, O. Corigliano, G. De Lorenzo, Strategic overview on fuel cell-based systems for mobility and electrolytic cells for hydrogen production, *Procedia Computer Science*, 2022, **200**, 1254-1263, doi: 10.1016/j.procs.2022.01.326.

[8] A. Al Rikabi, S. Abdelsalam, O. Y. Dabo, Hydrogen fuel cells for backup power applications: advantages, challenges, and case studies, *International Journal of Research in Advanced Engineering and Technology*, 2023, **9**, 25-30.

[9] V. Cigolotti, M. Genovese, P. Fragiacomo, Comprehensive review on fuel cell technology for stationary applications as sustainable and efficient poly-generation energy systems, *Energies*, 2021, **14**, 4963, doi: 10.3390/en14164963.

[10] H. Xing, C. Stuart, S. Spence, H. Chen, Fuel cell power systems for maritime applications: progress and perspectives, *Sustainability*, 2021, **13**, 1213, doi: 10.3390/su13031213.

[11] S. Kabir, S. Medina, G. Wang, G. Bender, S. Pylypenko, K. C. Neyerlin, Improving the bulk gas transport of Fe-N-C platinum group metal-free nanofiber electrodes via electrospinning for fuel cell applications, *Nano Energy*, 2020, **73**, 104791, doi: 10.1016/j.nanoen.2020.104791.

[12] I. Staffell, D. Scamman, A. Velazquez Abad, P. Balcombe, P. E. Dodds, P. Ekins, N. Shah, K. R. Ward, The role of hydrogen and fuel cells in the global energy system, *Energy & Environmental Science*, 2019, **12**, 463-491, doi: 10.1039/c8ee01157e.

[13] K. Turoń, Hydrogen-powered vehicles in urban transport systems - current state and development, *Transportation Research Procedia*, 2020, **45**, 835-841, doi: 10.1016/j.trpro.2020.02.086.

[14] Y. Manoharan, S. E. Hosseini, B. Butler, H. Alzhahrani, B. T. F. Senior, T. Ashuri, J. Krohn, Hydrogen fuel cell vehicles; current status and future prospect, *Applied Sciences*, 2019, **9**, 2296, doi: 10.3390/app9112296.

[15] T. H. Pham, Towards alkali-stable polymers and hydroxide exchange membranes functionalized with alicyclic quaternary ammonium cations, PhD Thesis, Centre for Analysis and Synthesis, Department of Chemistry, Lund University, 2019.

[16] A. C. Bhosale, P. C. Ghosh, L. Assaud, Preparation methods of membrane electrode assemblies for proton exchange membrane fuel cells and unitized regenerative fuel cells: a review, *Renewable and Sustainable Energy Reviews*, 2020, **133**, 110286, doi: 10.1016/j.rser.2020.110286.

[17] S. Du, W. Li, H. Wu, P.-Y. Abel Chuang, M. Pan, P.-C. Sui, Effects of ionomer and dispersion methods on rheological behavior of proton exchange membrane fuel cell catalyst layer ink, *International Journal of Hydrogen Energy*, 2020, **45**, 29430-29441, doi: 10.1016/j.ijhydene.2020.07.241.

[18] A. E. Yilmaz, M. M. Ispirli, An investigation on the parameters that affect the performance of hydrogen fuel cell, *Procedia - Social and Behavioral Sciences*, 2015, **195**, 2363-2369, doi: 10.1016/j.sbspro.2015.06.204.

[19] M. Ilbas, B. Kumuk, M. A. Alemu, B. Arslan, Numerical investigation of a direct ammonia tubular solid oxide fuel cell in comparison with hydrogen, *International Journal of Hydrogen Energy*, 2020, **45**, 35108-35117, doi: 10.1016/j.ijhydene.2020.04.060.

[20] Wei, Wu, Transition metal oxides as lithium-free cathodes

for solid-state lithium metal batteries, *Nano Energy*, 2020, **74**, 104867, doi: 10.1016/j.nanoen.2020.104867.

[21] Y. Ji, O. Kwon, O. S. Jeon, S. Yim, Y. Jeon, Y.-G. Shul, Effective single web-structured electrode for high membrane electrode assembly performance in polymer electrolyte membrane fuel cell, *Science Advances*, 2023, **9**, eadf4863, doi: 10.1126/sciadv.adf4863.

[22] L. Du, Y. Shao, J. Sun, G. Yin, J. Liu, Y. Wang, Advanced catalyst supports for PEM fuel cell cathodes, *Nano Energy*, 2016, **29**, 314-322, doi: 10.1016/j.nanoen.2016.03.016.

[23] M. Yandrasits, S. Hamrock, Poly(perfluorosulfonic acid) membranes. Polymer Science: A Comprehensive Reference. Amsterdam: Elsevier, 2012: 601-619, doi: 10.1016/b978-0-444-53349-4.00283-1.

[24] M. Isa, B. Ismail, I. Daut, M. R. Adzman, M. F. Mohammed, Characteristic and the efficiency of fuel cell, *American Journal of Applied Sciences*, 2006, **3**, 2167-2169, doi: 10.3844/ajassp.2006.2167.2169.

[25] H.-E. Kim, J. Kwon, H. Lee, Catalytic approaches towards highly durable proton exchange membrane fuel cells with minimized Pt use, *Chemical Science*, 2022, **13**, 6782-6795, doi: 10.1039/d2sc00541g.

[26] C. Gerling, M. Hanauer, U. Berner, K. Andreas Friedrich, PEM single cells under differential conditions: full factorial parameterization of the ORR and HOR kinetics and loss analysis, *Journal of the Electrochemical Society*, 2022, **169**, 014503, doi: 10.1149/1945-7111/ac44ba.

[27] X. Zhang, L. Truong-Phuoc, T. Asset, S. Pronkin, C. Pham-Huu, Are Fe-N-C electrocatalysts an alternative to Pt-based electrocatalysts for the next generation of proton exchange membrane fuel cells? *ACS Catalysis*, 2022, **12**, 13853-13875, doi: 10.1021/acscatal.2c02146.

[28] A. M. Andrade, Understanding the role of transition metals and metal oxides on carbon structures for enhancing electrocatalytic activity, 2021, PhD Thesis, University of California, Merced ProQuest Dissertations Publishing, 2021, 28717726.

[29] P. Luches, Ultrathin Transition Metal Oxide Films, Editor: Klaus Wandelt, Encyclopedia of Interfacial Chemistry, Elsevier, 2018, 388-397, doi: 10.1016/B978-0-12-409547-2.12869-0.

[30] L. Dubrovinsky, N. Dubrovinskaia, Transition metal oxides under extreme conditions. *Comprehensive Inorganic Chemistry II*, Amsterdam: Elsevier, 2013, 223-239, doi: 10.1016/b978-0-08-097774-4.00209-6.

[31] M. Schwarz, F. Faisal, S. Mohr, C. Hohner, K. Werner, T. Xu, T. Skála, N. Tsud, K. C. Prince, V. Matolín, Y. Lykhach, J. Libuda, Structure-dependent dissociation of water on cobalt oxide, *The Journal of Physical Chemistry Letters*, 2018, **9**, 2763-2769, doi: 10.1021/acs.jpclett.8b01033.

[32] S. Valeri, S. Benedetti, Synthesis and Preparation of Oxide Ultrathin Films, **2011**, 1-26, doi: 10.1002/9783527640171.ch1.

[33] C. N. R. Rao, Transition metal oxides, *Annual Review of Physical Chemistry*, 1989, **40**, 291-326, doi: 10.1146/annurev.pc.40.100189.001451.

[34] D. Nicholls, Introduction to the first-row transition elements. Complexes and First-Row Transition Elements. London: Macmillan Education UK, 1974, 120-127, doi: 10.1007/978-1-349-02335-6_9.

[35] Q. Luo, C. Lu, L. Liu, M. Zhu, A review on the synthesis of transition metal nitride nanostructures and their energy related applications, *Green Energy & Environment*, 2023, **8**, 406-437, https://doi.org/10.1016/j.gee.2022.07.002.

[36] C. Liu, Z. G. Neale, G. Cao, Understanding electrochemical potentials of cathode materials in rechargeable batteries, *Materials Today*, 2016, **19**, 109-123, doi: 10.1016/j.mattod.2015.10.009.

[37] Yangyang, Tan, Electronic tuning of confined sub-nanometer cobalt oxide clusters boosting oxygen catalysis and rechargeable Zn-air batteries, *Nano Energy*, 2021, **83**, 105813, doi: 10.1016/j.nanoen.2021.105813.

[38] X. Zhou, S. Tang, Y. Yin, S. Sun, J. Qiao, Hierarchical porous N-doped graphene foams with superior oxygen reduction reactivity for polymer electrolyte membrane fuel cells, *Applied Energy*, 2016, **175**, 459-467, doi: 10.1016/j.apenergy.2016.03.066.

[39] Y. Sun, G. Chen, S. Xi, Z. J. Xu, Catalytically influential features in transition metal oxides, *ACS Catalysis*, 2021, **11**, 13947-13954, doi: 10.1021/acscatal.1c04393.

[40] J. Murray, Independent learning project for advanced Chemistry, ILPAC I5 Transition Elements, 1-12.

[41] D. Jeong, J. Kim, O. Kwon, C. Lim, G. K. Jeeyoung Shin, Scandium doping effect on a layered perovskite cathode for low-temperature solid oxide fuel cells, *Applied Science*, 2018, **8**, 2217, doi: 10.3390/app8112217.

[42] M. S. Garapati, R. Sundara, Highly efficient and ORR active platinum-scandium alloy-partially exfoliated carbon nanotubes electrocatalyst for Proton Exchange Membrane Fuel Cell, *International Journal of Hydrogen Energy*, 2019, **44**, 10951-10963, doi: 10.1016/j.ijhydene.2019.02.161.

[43] M. K. Rath, A. Kossenko, A. Kalashnikov, M. Zinigrad, Novel anode current collector for hydrocarbon fuel solid oxide fuel cells, *Electrochimica Acta*, 2020, **331**, 135271, doi: 10.1016/j.electacta.2019.135271.

[44] C. Alegre, S. Siracusano, E. Modica, A. S. Aricò, V. Baglio, Titanium-tantalum oxide as a support for Pd nanoparticles for the oxygen reduction reaction in alkaline electrolytes, *Materials for Renewable and Sustainable Energy*, 2018, **7**, 1-10, doi: 10.1007/s40243-018-0114-z.

[45] E. Hornberger, A. Bergmann, H. Schmies, In situ stability studies of platinum nanoparticles supported on ruthenium–titanium mixed oxide (RTO) for fuel cell cathodes, *ACS Catal*, 2018, **8**, 9675-9683, doi: 10.1021/acscatal.8b02498.

[46] B. E. Hayden, Particle Size and Support Effects in Electrocatalysis, ACS Publications, 2013, **46**, 1858-1866, https://doi.org/10.1021/ar400001n.

[47] F. Papiya, P. Pattanayak, V. Kumar, S. Das, P. P. Kundu, Sulfonated graphene oxide and titanium dioxide coated with nanostructured polyaniline nanocomposites as an efficient cathode catalyst in microbial fuel cells, *Materials Science and Engineering: C*, 2020, **108**, 110498, doi:

10.1016/j.msec.2019.110498.

[48] K. M. Naik, E. Higuchi, H. Inoue, Two-dimensional oxygen-deficient TiO_2 nanosheets-supported Pt nanoparticles as durable catalyst for oxygen reduction reaction in proton exchange membrane fuel cells, *Journal of Power Sources*, 2020, **455**, 227972, doi: 10.1016/j.jpowsour.2020.227972.

[49] P. V, Prasadam, Atomic layer deposition of vanadium oxides: process and application review, *Materials Today Chemistry*, 2019, **12**, 396-423, doi: 10.1016/j.mtchem.2019.03.004.

[50] G. Bauer, V. Güther, H. Hess, A. Otto, O. Roidl, H. Roller, S. Sattelberger, Vanadium and Vanadium Compounds, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany, 2003, doi: 10.1002/14356007.a27.

[51] S. Ayyaru, S. Mahalingam, Y.-H. Ahn, A non-noble V_2O_5 nanorods as an alternative cathode catalyst for microbial fuel cell applications, *International Journal of Hydrogen Energy*, 2019, **44**, 4974-4984, doi: 10.1016/j.ijhydene.2019.01.021.

[52] J. Li, J. Hou, X. Xi, Y. Lu, M. Li, Y. Fan, L. Wang, L. Wang, X.-Z. Fu, J.-L. Luo, Cogeneration of ethylene and electricity in symmetrical protonic solid oxide fuel cells based on a $La_{0.6}Sr_{0.4}Fe_{0.8}Nb_{0.1}Cu_{0.1}O_{3-\delta}$ electrode, *Journal of Materials Chemistry A*, 2020, **8**, 25978-25985, doi: 10.1039/d0ta08974e.

[53] N. Kamyar, S. Rezaee, S. Shahrokhian, M. M. Amini, Direct conversion of inorganic complexes to platinum/thin oxide nanoparticles decorated on MOF-derived chromium oxide/nanoporous carbon composite as an efficient electrocatalyst for ethanol oxidation reaction, *Journal of Colloid and Interface Science*, 2019, **555**, 655-666, doi: 10.1016/j.jcis.2019.08.018.

[54] F. Shahbazi Farahani, B. Mecheri, M. Reza Majidi, M. A. Costa de Oliveira, A. D'Epifanio, F. Zurlo, E. Placidi, F. Arciprete, S. Licoccia, MnO_x-based electrocatalysts for enhanced oxygen reduction in microbial fuel cell air cathodes, *Journal of Power Sources*, 2018, **390**, 45-53, doi: 10.1016/j.jpowsour.2018.04.030.

[55] S. S. Ahmad Shah, T. Najam, C. Cheng, S. Chen, R. Xiang, L. Peng, L. Lu, W. Ding, Z. Wei, Design and synthesis of conductive carbon polyhedrons enriched with Mn-Oxide active-centres for oxygen reduction reaction, *Electrochimica Acta*, 2018, **272**, 169-175, doi: 10.1016/j.electacta.2018.04.008.

[56] M. R. Majidi, F. Shahbazi Farahani, M. Hosseini, I. Ahadzadeh, Low-cost nanowired α-MnO_2/C as an ORR catalyst in air-cathode microbial fuel cell, *Bioelectrochemistry*, 2019, **125**, 38-45, doi: 10.1016/j.bioelechem.2018.09.004.

[57] J. Ding, P. Kannan, P. Wang, S. Ji, H. Wang, Q. Liu, H. Gai, F. Liu, R. Wang, Synthesis of nitrogen-doped MnO/carbon network as an advanced catalyst for direct hydrazine fuel cells, *Journal of Power Sources*, 2019, **413**, 209-215, doi: 10.1016/j.jpowsour.2018.12.050.

[58] S. Das, I. Chakraborty, P. P. Rajesh, M. M. Ghangrekar, Performance evaluation of microbial fuel cell operated with Pd or MnO_2 as cathode catalyst and *Chaetoceros* pretreated anodic inoculum, *Journal of Hazardous, Toxic, and Radioactive Waste*, 2020, **24**, 1-7, doi: 10.1061/(asce)hz.2153-5515.0000501.

[59] Y. Yang, Y. Wang, Y. Xiong, X. Huang, L. Shen, R. Huang, H. Wang, J. P. Pastore, S.-H. Yu, L. Xiao, J. D. Brock, L. Zhuang, H. D. Abruña, *in situ* X-ray absorption spectroscopy of a synergistic Co-Mn oxide catalyst for the oxygen reduction reaction, *Journal of the American Chemical Society*, 2019, **141**, 1463-1466, doi: 10.1021/jacs.8b12243.

[60] Carlos, C. Lima, Enhancing the methanol tolerance of ultrasmall platinum nanoparticles and Manganese oxide onto carbon for direct methanol fuel cell: the importance of the synthesis procedure, *Electrochimica Acta*, 2020, **363**, 137256, doi: 10.1016/j.electacta.2020.137256.

[61] A. Devi Sekar, T. Jayabalan, H. Muthukumar, N. I. Chandrasekaran, S. N. Mohamed, M. Matheswaran, Enhancing power generation and treatment of dairy waste water in microbial fuel cell using Cu-doped iron oxide nanoparticles decorated anode, *Energy*, 2019, **172**, 173-180, doi: 10.1016/j.energy.2019.01.102.

[62] C. Santoro, A. Serov, L. Stariha, M. Kodali, J. Gordon, S. Babanova, O. Bretschger, K. Artyushkova, P. Atanassov, Iron based catalysts from novel low-cost organic precursors for enhanced oxygen reduction reaction in neutral media microbial fuel cells, *Energy & Environmental Science*, 2016, **9**, 2346-2353, doi: 10.1039/c6ee01145d.

[63] A. M. Gorlova, O. V. Komova, O. V. Netskina, O. A. Bulavchenko, I. L. Lipatnikova, V. I. Simagina, Hydrogen for fuel cells: effect of copper and iron oxides on the catalytic hydrolysis and hydrothermolysis of ammonia borane, *Russian Journal of Electrochemistry*, 2020, **56**, 170-173, doi: 10.1134/s1023193520020044.

[64] W.-J. Wang, F. Roberts, S. Peterson, S. Ha, L. Scudiero, R. Coustel, M. Mallet, M. Abdelmoula, C. Ruby, Iron-iron oxide supported palladium catalyst for the interconversion of formate and carbon dioxide, *Chemical Engineering Journal*, 2022, **427**, 131763, doi: 10.1016/j.cej.2021.131763.

[65] J. Liu, H. Bao, B. Zhang, Q. Hua, M. Shang, J. Wang, L. Jiang, Geometric occupancy and oxidation state requirements of cations in cobalt oxides for oxygen reduction reaction, *ACS Applied Materials & Interfaces*, 2019, **11**, 12525-12534, doi: 10.1021/acsami.9b00481.

[66] H. M. Abd El-Lateef, N. F. Almulhim, A. A. Alaulamie, M. M. Saleh, I. M. A. Mohamed, Design of ultrafine nickel oxide nanostructured material for enhanced electrocatalytic oxidation of urea: Physicochemical and electrochemical analyses, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2020, **585**, 124092, doi: 10.1016/j.colsurfa.2019.124092.

[67] X. Fuku, M. Modibedi, N. Matinise, P. Mokoena, N. Xaba, M. Mathe, Single step synthesis of bio-inspired NiO/C as Pd support catalyst for dual application: alkaline direct ethanol fuel cell and CO_2 electro-reduction, *Journal of Colloid and Interface Science*, 2019, **545**, 138-152, doi: 10.1016/j.jcis.2019.03.030.

[68] H. Wang, L. Lu, P. Subramanian, S. Ji, P. Kannan, Co, Fe-ions intercalated $Ni(OH)_2$ network-like nanosheet arrays as highly efficient non-noble catalyst for electro-oxidation of urea, *International Journal of Hydrogen Energy*, 2021, **46**, 34318-34332, doi: 10.1016/j.ijhydene.2021.08.022.

[69] S. M. Pawar, J. Kim, A. I. Inamdar, H. Woo, Y. Jo, B. S. Pawar, S. Cho, H. Kim, H. Im, Multi-functional reactively-

sputtered copper oxide electrodes for supercapacitor and electrocatalyst in direct methanol fuel cell applications, *Scientific Reports*, 2016, **6**, 21310, doi: 10.1038/srep21310.

[70] Y. Gu, J.-J. Tao, T. Wang, Y.-H. Liu, B.-F. Peng, L.-Y. Zhu, H.-L. Lu, Nonlinear growth of zinc tin oxide thin films prepared by atomic layer deposition, *Ceramics International*, 2021, **47**, 22760-22767, doi: 10.1016/j.ceramint.2021.04.294.

[71] J. Zheng, T. Zhang, H. Zeng, W. Guo, B. Zhao, Y. Sun, Y. Li, L. Jiang, Methanol detection: multishelled hollow structures of yttrium oxide for the highly selective and ultrasensitive detection of methanol (small 9/2019), *Small*, 2019, **15**, 1970049, doi: 10.1002/smll.201970049.

[72] J. Yang, X. Li, Y. Cheng, C. Fan, C. Pan, B. Huang, X. Meng, J. Zhang, A. Zheng, X. Ma, L. Guo, R. Luque, W. Zhang, Y. Sun, Efficient and selective aqueous photocatalytic mono-dehydration of sugar alcohols using functionalized yttrium oxide nanocatalysts, *Green Chemistry*, 2020, **22**, 5333-5344, doi: 10.1039/d0gc00914h.

[73] W. Sun, L. Zheng, Y. Wang, D. Li, Z. Liu, L. Wu, T. Fang, J. Wu, A study for thermodynamics and experiment on direct synthesis of dimethyl carbonate from carbon dioxide and methanol over yttrium oxide, *Industrial & Engineering Chemistry Research*, 2020, **59**, 4281–4290, doi: 10.1021/acs.iecr.9b06092.

[74] V. Murugavalli, R. Abirami, P. Dhanalakshmi, G. Rathika, S. Abinaya, R. Abinaya, A. Ayeshamariam, M. Jayachandran, Zirconium oxide doped with hafnium oxide by hydrothermal method, *Evolution in Polymer Technology Journal*, 2018, **1**, 180002.

[75] Fuel Cell Handbook, EG&G Technical Services, U.S. Department of Energy Office of Fossil Energy National Energy Technology Laboratory P.O. Box 880 Morgantown, West Virginia, 2004, 26507-0880, doi: 10.1016/s0031-9422(00)82398-5.

[76] J. I. Eastcott, A. Parakh, M. T. Y. Paul, A. W. H. Lee, M. W. Bilton, B. D. Gates, Nanoscale thin films of niobium oxide on platinum surfaces: creating a platform for optimizing material composition and electrochemical stability, *Canadian Journal of Chemistry*, 2018, **96**, 260-266, doi: 10.1139/cjc-2017-0595.

[77] L. Chinchilla, D. Rossouw, T. Trefz, D. Susac, N. Kremliakova, G. A. Botton, Nanoscale analysis of structural and chemical changes in aged hybrid Pt/NbO x/C fuel cell catalysts, *Journal of Power Sources*, 2017, **356**, 140-152, doi: 10.1016/j.jpowsour.2017.04.017.

[78] A. M. Jasim, G. Xu, S. Al-Salihi, Y. Xing, Dense niobium oxide coating on carbon black as a support to platinum electrocatalyst for oxygen reduction, *ChemistrySelect*, 2020, **5**, 11431-11437, doi: 10.1002/slct.202003225.

[79] S. H. Ammar, M. D. Salman, R. F. Shafi, Catalytic activity of niobium oxide supported bimetallic nanocatalysts (Ir_xPt_{1-x}/Nb_2O_5) for oxidation of formaldehyde at moderate temperature, *Colloid and Interface Science Communications*, 2020, **38**, 100305, doi: 10.1016/j.colcom.2020.100305.

[80] A. Omidvar, Catalytic role of transition metals supported on niobium oxide in O_2 activation, *Applied Surface Science*, 2018, **434**, 1239-1247, doi: 10.1016/j.apsusc.2017.11.239.

[81] Changlai, Wang, Engineering the coordination environment enables molybdenum single-atom catalyst for efficient oxygen reduction reaction, *Journal of Catalysis*, 2020, **389**, 150-156, doi: 10.1016/j.jcat.2020.05.034.

[82] W. Sung, J.-W. Choi, A membraneless microscale fuel cell using non-noble catalysts in alkaline solution, *Journal of Power Sources*, 2007, **172**, 198-208, doi: 10.1016/j.jpowsour.2007.07.012.

[83] D. M. A. Latif, I. H. Shallal, A. A. Shuihab, H. Shallal, A. A. Shuihab, Synthesis and study of some physical properties of cadmium The and 15th study Synthesis of some physical properties of cadmium oxide CdO thin films oxide CdO thin films Assessing the feasibility of using the heat demand-outdoor Aliyah heat temperature fun, *Energy Procedia*, 2019, **157**, 611–618, doi: 10.1016/j.egypro.2018.11.226.

[84] J. Chang, R. S. Mane, D. Ham, W. Lee, B. W. Cho, J. K. Lee, S.-H. Han, Electrochemical capacitive properties of cadmium oxide films, *Electrochimica Acta*, 2007, **53**, 695-699, doi: 10.1016/j.electacta.2007.07.056.

[85] J. L. Pineda-Delgado, C. K. Gutierrez B, S. Rivas, N. Arjona, L. G. Arriaga, A. U. Chávez-Ramirez, Synthesis and evaluation of HfO_2 as a prospective filler in inorganic-organic hybrid membranes based on Nafion for PEM fuel cells, *Nanotechnology*, 2019, **30**, 105707, doi: 10.1088/1361-6528/aaf7c2.

[86] J.-W. Jung, G.-Y. Kim, N.-W. Lee, W.-H. Ryu, Low-temperature synthesis of tetragonal phase of hafnium oxide using polymer-blended nanofiber precursor, *Applied Surface Science*, 2020, **533**, 147496, doi: 10.1016/j.apsusc.2020.147496.

[87] H. Shirai, N. Nunotani, N. Imanaka, Photocatalytic hydrogen evolution from water over hafnium oxyphosphate, *Journal of the Ceramic Society of Japan*, 2019, **127**, 700-702, doi: 10.2109/jcersj2.19059.

[88] A.A. Alharbi, N.B. Alqahtani, A.M. Alkhedhair, A.J. Alabduly, A.A. Almaleki, M.H. Almadih, M.S. Albishi, A.A. Almayeef, A Developed Plasmatron Design to Enhance Production of Hydrogen in Synthesis Gas Produced by a Fuel Reformer System, *Energies*, 2022, **15**, 1071, doi: 10.3390/en15031071.

[89] You-Dong, Kim, Stable ceria-based electrolytes for intermediate temperature-solid oxide fuel cells via hafnium oxide blocking layer, *Journal of Alloys and Compounds*, 2019, **779**, 121-128, doi: 10.1016/j.jallcom.2018.11.069.

[90] X. Yang, F. Zhao, Y.-W. Yeh, R. S. Selinsky, Z. Chen, N. Yao, C. G. Tully, Y. Ju, B. E. Koel, Nitrogen-plasma treated hafnium oxyhydroxide as an efficient acid-stable electrocatalyst for hydrogen evolution and oxidation reactions, *Nature Communications*, 2019, **10**, 1543, doi: 10.1038/s41467-019-09162-5.

[91] L. Mariscal-Becerra, M. C. Flores-Jiménez, J. M. Hernández-Álcantara, E. Camarillo, C. Falcony-Guajardo, R. Vázquez-Arreguín, H. Murrieta Sanchez, Structural and luminescent analysis of hafnium-doped yttrium oxide and yttrium-doped hafnium oxide powders and doped with trivalent europium and terbium ions, *Journal of Nanophotonics*, 2018, **12**, 036013-036013, doi: 10.1117/1.jnp.12.036013.

[92] I. Villa, A. Lauria, F. Moretti, M. Fasoli, C. Dujardin, M. Niederberger, A. Vedda, Radio-luminescence spectral features and fast emission in hafnium dioxide nanocrystals, *Physical Chemistry Chemical Physics*, 2018, **20**, 15907-15915, doi: 10.1039/c8cp01230j.

[93] N, Samsudin, Deposition and characterization of RF-sputtered-Ta_2O_5 thin films for O_2 reduction reaction in polymer electrolyte membrane fuel cells (PEMFC), *Optik*, 2018, **170**, 295-303, doi: 10.1016/j.ijleo.2018.05.106.

[94] F. Amano, Y. Furusho, Y.-M. Hwang, Amorphous iridium and tantalum oxide layers coated on titanium felt for electrocatalytic oxygen evolution reaction, *ACS Applied Energy Materials*, 2020, **3**, 4531-4538, doi: 10.1021/acsaem.0c00208.

[95] S. Kim, Capacitance response characteristics of hydrogen sensor with tantalum oxide dielectric layer, *International Journal of Hydrogen Energy*, 2018, **43**, 19810-19815, doi: 10.1016/j.ijhydene.2018.08.187.

[96] Y. Zhao, L. Wu, K. Zhou, J. Lang, G. Wang, P. Tian, X. Wang, Palladium-loaded tantalum oxide modified Pt electrode toward electrochemical oxidation of ethylene glycol, *Journal of Electroanalytical Chemistry*, 2019, **839**, 166-172, doi: 10.1016/j.jelechem.2019.03.006.

[97] H. Tian, X. Cui, J. Shi, Emerging electrocatalysts for PEMFCs applications : Tungsten oxide as an example, *Chemical Engineering Journal*, 2021, **421**, 129430, doi: 10.1016/j.cej.2021.129430.

[98] S. Das, M. M. Ghangrekar, Tungsten oxide as electrocatalyst for improved power generation and wastewater treatment in microbial fuel cell, *Environmental Technology*, 2020, **41**, 2546-2553, doi: 10.1080/09593330.2019.1575477.

[99] I. Das, M. T. Noori, G. D. Bhowmick, M. M. Ghangrekar, Synthesis of tungstate oxide/bismuth tungstate composite and application in microbial fuel cell as superior low-cost cathode catalyst than platinum, *Journal of the Electrochemical Society*, 2018, **165**, G146-G153, doi: 10.1149/2.0781813jes.

[100] S. M. Brkovic, V. M. Nikolic, M. Marceta Kaninski, I. A. Pasti, Pt/C catalyst impregnated with tungsten-oxide- Hydrogen oxidation reaction Vs CO tolerance, *International Journal of Hydrogen Energy*, 2019, **44**, 13364-13372, doi: 10.1016/j.ijhydene.2019.03.270.

[101] K. Nose, T.H. Okabe, Platinum Group Metals Production, in: S. Seetharaman (Eds.), Treatise on Process Metallurgy, Elsevier, 2014, **3**, 1071-1097, doi: 10.1016/b978-0-08-096988-6.00018-3.

[102] S. Samad, K. S. Loh, W. Y. Wong, T. K. Lee, J. Sunarso, S. T. Chong, W. R. Wan Daud, Carbon and non-carbon support materials for platinum-based catalysts in fuel cells, *International Journal of Hydrogen Energy*, 2018, **43**, 7823-7854, doi: 10.1016/j.ijhydene.2018.02.154.

[103] L. Huang, S. Zaman, X. Tian, Z. Wang, W. Fang, B. Y. Xia, Advanced platinum-based oxygen reduction electrocatalysts for fuel cells, *Accounts of Chemical Research*, 2021, **54**, 311-322, doi: 10.1021/acs.accounts.0c00488.

[104] N. Basu, N. S. Sterin, S. R. Mamidala, A. Shenoy, N. Bhat, Optimization of Platinum dioxide properties by plasma oxidation of sputtered PtO_x, *Materialia*, 2019, **8**, 100477, doi: 10.1016/j.mtla.2019.100477.

[105] R. A. Gonçalves, M. R. Baldan, E. G. Ciapina, O. M. Berengue, Nanostructured Pd/Sb_2O_3: A new and promising fuel cell electrocatalyst and non-enzymatic amperometric sensor for ethanol, *Applied Surface Science*, 2019, **491**, 9-15, doi: 10.1016/j.apsusc.2019.06.116.

[106] S. Chung, D. H. Seo, M. Choi, X. Mao, A. Du, K. Ham, S. Giddey, J. Lee, H. Ju, Rhodium-molybdenum oxide electrocatalyst with dual active sites for electrochemical ammonia synthesis under neutral pH condition, *Journal of Electroanalytical Chemistry*, 2021, **896**, 115157, doi: 10.1016/j.jelechem.2021.115157.

[107] C.-Y. Ahn, S. Y. Kang, H. J. Choi, O.-H. Kim, Y.-E. Sung, Y.-H. Cho, Effect of anode iridium oxide content on the electrochemical performance and resistance to cell reversal potential of polymer electrolyte membrane fuel cells, *International Journal of Hydrogen Energy*, 2021, **46**, 14713-14723, doi: 10.1016/j.ijhydene.2021.01.199.

[108] T. Labi, F. Van Schalkwyk, S. M. Andersen, P. Morgen, S. C. Ray, J. Chamier, Increasing fuel cell durability during prolonged and intermittent fuel starvation using supported IrO_x, *Journal of Power Sources*, 2021, **490**, 229568, doi: 10.1016/j.jpowsour.2021.229568.

[109] D. Nkomo, A. Mwamba, Beneficiation opportunities for osmium: a review, *IOP Conference Series*: *Materials Science and Engineering*, 2020, **839**, 012014, doi: 10.1088/1757-899x/839/1/012014.

[110] A. M. Asiri, K. Akhtar, S. B. Khan, Cobalt oxide nanocomposites and their electrocatalytic behavior for oxygen evolution reaction, *Ceramics International*, 2019, **45**, 13340-13346, doi: 10.1016/j.ceramint.2019.04.028.

[111] L. Gong, X. Y. E. Chng, Y. Du, S. Xi, B. S. Yeo, Enhanced catalysis of the electrochemical oxygen evolution reaction by iron(III) ions adsorbed on amorphous cobalt oxide, *ACS Catalysis*, 2018, **8**, 807-814, doi: 10.1021/acscatal.7b03509.

[112] I. Alves, J. Santos, D. Viégas, E. Marques, C. Lacerda, L. Zhang, J. Zhang, A. Marques, Nanoparticles of Fe_2O_3 and Co_3O_4 as efficient electrocatalysts for oxygen reduction reaction in acid medium, *Journal of the Brazilian Chemical Society*, 2019, **30**, 2681-2690, doi: 10.21577/0103-5053.20190195.

[113] M. B. Askari, P. Salarizadeh, A. Di Bartolomeo, M. H. Ramezan zadeh, H. Beitollahi, S. Tajik, Hierarchical nanostructures of $MgCo_2O_4$ on reduced graphene oxide as a high-performance catalyst for methanol electro-oxidation, *Ceramics International*, 2021, **47**, 16079-16085, doi: 10.1016/j.ceramint.2021.02.182.

[114] J. Jaafar, M. H. D. Othman, A. F. Ismail, M. A. Rahman, N. Yusof, F. Aziz, Electro-spun of novel PVDF-Pt-Pd/RGO-CeO_2 composite nanofibers as the high potential of robust anode catalyst in direct methanol fuel cell: fabrication and characterization, *Inorganic Chemistry Communications*, 2019, **107**, 107487, doi: 10.1016/j.inoche.2019.107487.

[115] F. Papiya, P. Pattanayak, A. K. Biswas, P. P. Kundu,

Polyaniline and sulfonated graphene oxide supported bimetallic Manganese cobalt oxides as an effective and non-precious cathode catalyst in air-cathode microbial fuel cells, *Journal of Environmental Chemical Engineering*, 2021, **9**, 105992, doi: 10.1016/j.jece.2021.105992.

[116] K. Maiti, J. Balamurugan, J. Gautam, N. H. Kim, J. H. Lee, Hierarchical flowerlike highly synergistic three-dimensional iron tungsten oxide nanostructure-anchored nitrogen-doped graphene as an efficient and durable electrocatalyst for oxygen reduction reaction, *ACS Applied Materials & Interfaces*, 2018, **10**, 32220-32232, doi: 10.1021/acsami.8b11406.

[117] A. Caglar, M. S. Cogenli, A. B. Yurtcan, O. Alal, H. Kivrak, Remarkable activity of a ZnPdPt anode catalyst: synthesis, characterization, and formic acid fuel cell performance, *Journal of Physics and Chemistry of Solids*, 2021, **156**, 110163, doi: 10.1016/j.jpcs.2021.110163.

[118] Ling, Sun, Chemical activation of commercial CNTs with simultaneous surface deposition of Manganese oxide nano flakes for the creation of CNTs-graphene supported oxygen reduction ternary composite catalysts applied in air fuel cell, *Applied Surface Science*, 2018, **447**, 518-527, doi: 10.1016/j.apsusc.2018.04.025.

[119] F. Shahbazi Farahani, A. D'Epifanio, M. R. Majidi, E. Placidi, F. Arciprete, B. Mecheri, Tailoring morphology and structure of Manganese oxide nanomaterials to enhance oxygen reduction in microbial fuel cells, *Synthetic Metals*, 2020, **268**, 116487, doi: 10.1016/j.synthmet.2020.116487.

[120] Elancheziyan, Mari, Efficient electro-catalytic oxidation of ethylene glycol using flower-like graphitic carbon nitride/iron oxide/palladium nanocomposite for fuel cell application, *Fuel*, 2020, **280**, 118646, doi: 10.1016/j.fuel.2020.118646.

[121] D. Sun, S. Tian, C. Yin, F. Chen, J. Xie, C. Huang, C. Li, Thin Film Deposition Techniques in Surface Engineering Strategies for Advanced Lithium-Ion Batteries, *Coatings*, 2023, **13**, 505, doi: 10.3390/coatings13030505.

[122] R. S. Pedanekar, S. K. Shaikh, K. Y. Rajpure, Thin film photocatalysis for environmental remediation: a status review, *Current Applied Physics*, 2020, **20**, 931-952, doi: 10.1016/j.cap.2020.04.006.

[123] B. K. Das, Growth of ZnO thin film on silicon and glass substrate by pulsed laser deposition technique, *SSRN Electronic Journal*, 2021, doi: 10.2139/ssrn.3840984.

[124] H. H. Sønsteby, T. Aarholt, Ø. Prytz, H. Fjellvåg, O. Nilsen, First complex oxide superconductor by atomic layer deposition, *Chemical Communications*, 2018, **54**, 8253-8256, doi: 10.1039/c8cc04998j.

[125] S. Schlicht, K. Percin, S. Kriescher, A. Hofer, C. Weidlich, M. Wessling, J. Bachmann, Atomic layer deposition for efficient oxygen evolution reaction at Pt/Ir catalyst layers, *Beilstein Journal of Nanotechnology*, 2020, **11**, 952-959, doi: 10.3762/bjnano.11.79.

[126] R. Alfred Maarten Coetzee, T.-C. Jen, M. Bhamjee, J. Lu, The mechanistic process analysis and temperature effect in a low pressure square type atomic layer deposition reactor, *International Journal of Mechanical Engineering and Robotics Research*, 2019, **8**, 792-796, doi: 10.18178/ijmerr.8.5.792-796.

[127] K. Väyrynen, T. Hatanpää, M. Mattinen, M. Heikkilä, K. Mizohata, K. Meinander, J. Räisänen, M. Ritala, M. Leskelä, Diamine adduct of cobalt(II) chloride as a precursor for atomic layer deposition of stoichiometric cobalt(II) oxide and reduction thereof to cobalt metal thin films, *Chemistry of Materials*, 2018, **30**, 3499-3507, doi: 10.1021/acs.chemmater.8b01271.

[128] E. Riyanto, E. Martides, E. Junianto, B. Prawara, The growth mechanisms of atomic layer deposition: an overview, *Eksergi*, 2020, **17**, 56-61, doi: 10.31315/e.v17i2.3714.

[129] D. Raj, F. Scaglione, G. Fiore, F. Celegato, P. Rizzi, Nanostructured molybdenum oxides from aluminium-based intermetallic compound: synthesis and application in hydrogen evolution reaction, *Nanomaterials*, 2021, **11**, 1313, doi: 10.3390/nano11051313.

[130] B. Cottis, M. Graham, R. Lindsay, S. Lyon, T. Richardson, D. Scantlebury, & H. Stott, *Shreir's Corrosion*, Elsevier BV, The Netherlands, 2010.

[131] E. Petrucci, M. Orsini, F. Porcelli, S. De Santis, G. Sotgiu, Effect of spin coating parameters on the electrochemical properties of ruthenium oxide thin films, *Electrochem*, 2021, **2**, 83-94, doi: 10.3390/electrochem2010008.

[132] S. Hernández, C. Ottone, S. Varetti, M. Fontana, D. Pugliese, G. Saracco, B. Bonelli, M. Armandi, Spin-coated *vs.* electrodeposited Mn oxide films as water oxidation catalysts, *Materials*, 2016, **9**, 296, doi: 10.3390/ma9040296.

[133] W. Belhadj, A. Timoumi, F. A. Alamer, O. H. Alsalmi, S. N. Alamri, Experimental study and theoretical modeling of coating-speed-dependent optical properties of TiO_2-graphene-oxide thin films, *Results in Physics*, 2021, **30**, 104867, doi: 10.1016/j.rinp.2021.104867.