

Review

Oxygen electrocatalysis in chemical energy conversion and storage technologies

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ABSTRACT

Oxygen electrocatalysis that we first defined is considered as the most important phenomenon in almost all electrochemical industries because it is the most sluggish reaction that governs the overall reaction rate in electrochemical cells. In this review, we cover two main areas of oxygen–water electrocatalysis, oxygen reduction to water and oxygen evolution from water. In particular, it aims to provide the readers with an understanding of the critical scientific challenges facing the development of oxygen electrocatalysts, various unique attributes of recent novel catalysts, the latest developments in electrode construction and the outlook for future generation of oxygen electrocatalysts. This review will be of value to both electrochemists and other applied scientists interested in this field of electrocatalysis.

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1. Introduction

Oxygen (O₂) electrochemistry is a description of the electrocatalytic reduction and evolution of molecular oxygen. In oxygen reduction reaction (ORR), O₂ molecule combines with electrons to form a product, whereas oxygen evolution reaction (OER) generates O₂ molecule by taking electrons away from a reactant. O₂

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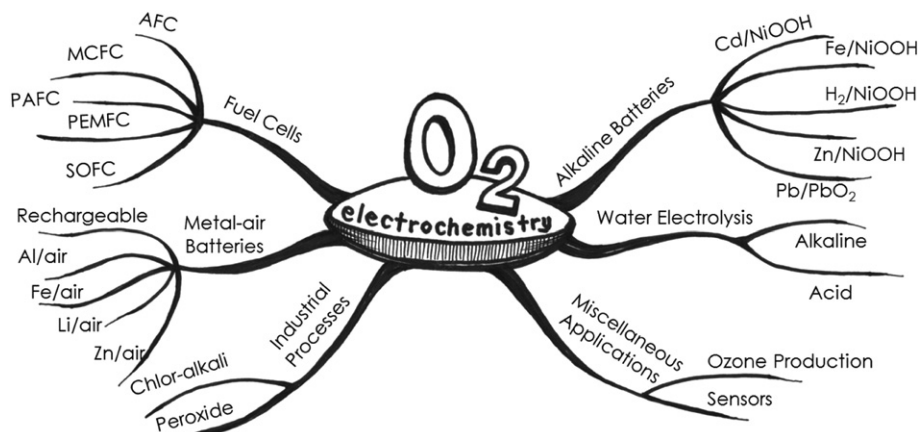
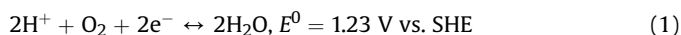


Fig. 1. Mind map of oxygen electrochemical technologies and processes where O₂ electrochemistry plays a vital role.

electrochemistry has been extensively and intensively studied because of its fundamental complexity and importance in many practical technologies and industrial processes [1] (Fig. 1). In particular, it is at the heart of several renewable energy technologies such as water electrolysis, metal–air batteries, fuel cells and other industrial applications.

O₂ electrocatalysis is a phenomenon in which the rate of these ORRs and OERs is promoted at the electrode surface polarized by an electrical potential. To elucidate the notion of O₂ electrocatalysis, we introduce a heuristic example, the electrochemical redox reaction of water in highly acidic liquid media,



This redox reaction is in thermodynamic equilibrium at the electrode surface at a potential of 1.23 V. It means that the rate of forward reaction is the same as the rate of backward reaction so that there is no net current reaction. When the electrical potential departs from the equilibrium potential in a positive direction, the electrons move from the water molecule to the electrode, thus we observe an oxidation (anodic) current due to water oxidation to form O₂ at the electrode surface. On the contrary, as the electrical potential moves in negative direction, the electrons move from the electrode to solution, we observe a reduction (cathodic) current by O₂ reduction to produce water. The additional potential necessary to drive the electric current through electrochemical reaction is termed as overpotential [2]. The overpotential needed to cause a certain current primarily depends on electrode material. For example, platinum (Pt) is well-known as the best electrocatalyst for an ORR to water reaction, while gold (Au) electrode shows much lower current at the same overpotential than Pt in the ORR [1].

Among various reactions in O₂ electrochemistry, ORR to water and OER from water (Eq. (1)) are major interests these days because these reactions are well-known bottlenecks that limit power density of hydrogen (H₂) fuel cell and energy efficiency of water electrolysis even when facilitated by comparatively highly active, but very expensive precious metal catalysts. In this context, the design of cost-effective and highly active electrocatalysts for energy storage applications is a crucial component for the future dream of carbon-neutral hydrogen energy economy.

Moreover, successful development of O₂ electrocatalysts will lead the electrochemistry discipline to more complex problems like electrochemical CO₂ recycling to hydrocarbon synthesis and direct electricity generation from electrochemical fuel oxidation, which requires the understanding of electrochemistry of more complicated hydrocarbon-based organic materials [3].

In this review, we mainly introduce the researches on water-producing ORR in fuel cells and water-splitting OER in water electrolysis. We will use the term O₂ electrocatalysis in lieu of O₂–H₂O electrochemistry since most electrocatalytic processes occur in aqueous solutions. In addition, we will also introduce the studies on bi-functional O₂ catalysts that are important in metal–air batteries and unitized regenerative fuel cells (URFCs). Finally, we provide some perspectives on the status of research on ORR and OER catalysts and the anticipated future research direction of O₂ electrochemistry.

2. Understanding oxygen electrocatalysts and its industrial applications

2.1. Oxygen reduction reaction

There are two main streams in the development of ORR catalysts for the low-temperature fuel cell cathode, one is reduction of the Pt amount in cathode while keeping the same level of power density and the other is searching for a new inexpensive material with the activity and durability comparable to Pt. In this section, we introduce the development history of Pt-based catalysts and non-Pt based catalysts for oxygen reduction summarized as the timelines depicted in Fig. 2.

2.1.1. Pt-based alloy catalysts

Döbereiner first discovered heterogeneous Pt catalysis for oxygen reduction and simultaneously hydrogen oxidation to form water in 1823 [4]. Based on the discovery of Pt catalysis and the development of electrochemistry, Grove first invented H₂–O₂ fuel cell using Pt as catalysts for hydrogen oxidation and oxygen reduction (Fig. 3) [5]. However, fuel cell technology has been out of interest over the past one hundred years after the first invention because of the usage of cheap and powerful steam engines and internal combustion engines based on fossil fuel. Of late, the concern of global warming and fossil fuel depletion rekindled interest in ecofriendly fuel cell technology.

The most important requisites of a catalyst are activity, stability, selectivity to the target reaction, and cost. Because of the sluggish reaction rate of ORR at the fuel cell cathode which has been a challenging stone wall for the commercialization of the low-temperature fuel cell, the basic research on the reaction mechanism and the extensive search for the active electrocatalyst were performed during 1960s and 1970s. The first attempt of fuel cell commercialization was phosphoric acid fuel cell (PAFC) developed by United Technology Corporation (UTC) in 1970s. This has driven

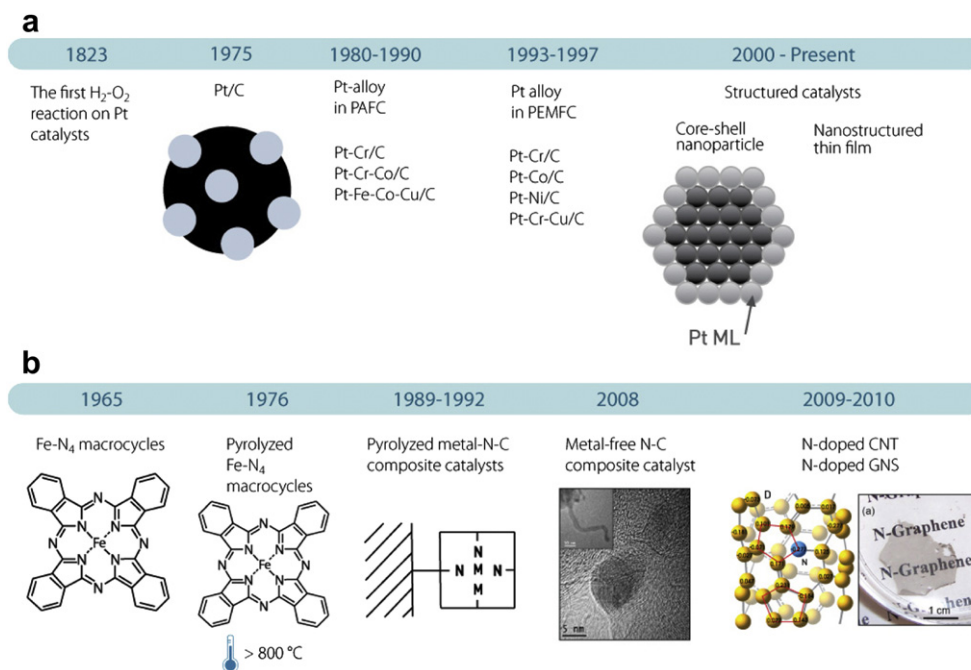


Fig. 2. Brief history of ORR catalysts for (a) Pt-based and (b) N–C based catalysts (reprinted with permissions from [26] Copyright 1989 Springer, [29] Copyright 2008 Elsevier, [30] Copyright 2009 AAAS, [31] Copyright 2010 ACS).

extensive R&D in Pt-based electrocatalyst for ORR to improve its activity and stability, since Pt was widely accepted as the best catalyst.

The polytetrafluoroethylene (PTFE)-bonded Pt supported on carbon black developed by Kunz and Gruver at UTC in 1975 was a giant leap in the advancement of fuel cell catalysts (Fig. 4). The carbon support provides four advantages in the performance of the catalysts [6].

- (1) Uniform dispersion of highly loaded catalysts on the support
- (2) Good electrical conductivity
- (3) Chemical stability of support material
- (4) Prevention of Pt agglomeration

There had been further studies on carbon supported Pt-alloy ORR catalysts in the PAFC application at UTC until 1990. The first

binary catalyst was reported in the patent issued to Jalan in 1980 [7] and Pt–V/C showed improved activity and durability for ORR compared to a pure Pt catalyst. Then, the first ternary catalyst of Pt–Cr–Co/C developed by the same research group was found to be more active and more stable in PAFC system [8]. In addition, there

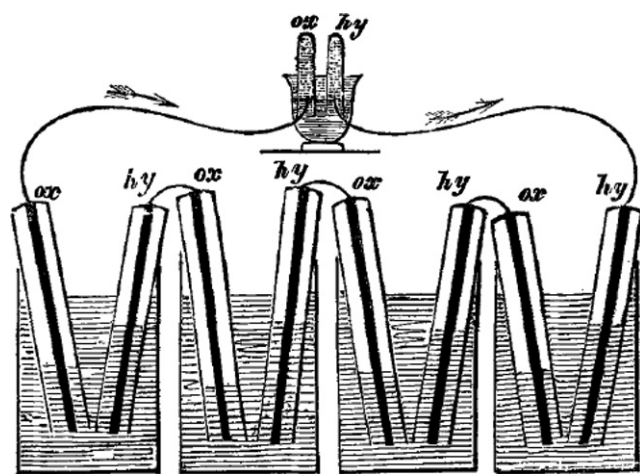


Fig. 3. The first H_2 - O_2 fuel cell invented by Grove (copied with permission from the "Electrochemical Science and Technology Information Resource" (ESTIR) (<http://electrochem.cwrui.edu/estir/>) on "08/14/2012". The original material is subject to periodical changes and updates) [5].

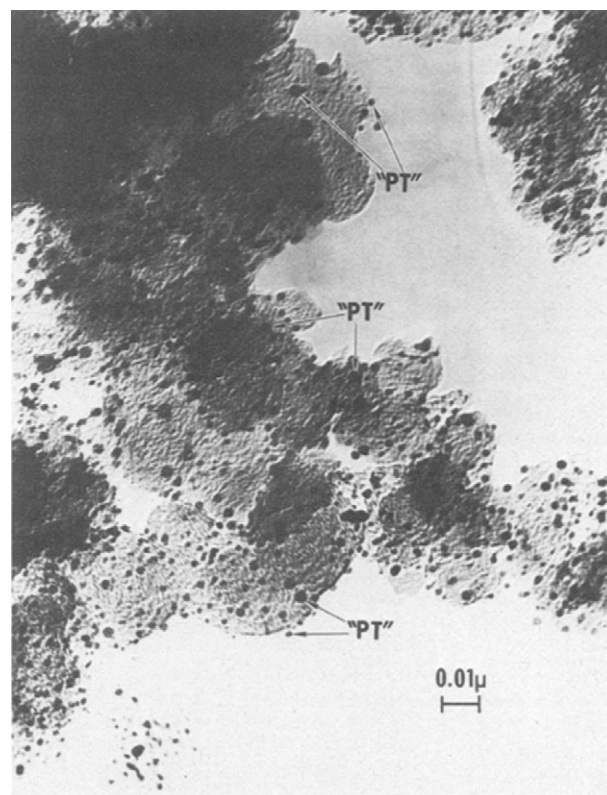


Fig. 4. Electron photomicrograph of Pt supported on Vulcan XC-72 (reprinted with permission from [6], Copyright 1975 The Electrochemical Society).

was an attempt to fabricate quaternary Pt-alloy, Pt–Fe–Co–Cu/C, in NEChemCat [9].

Since the polymer electrolyte membrane fuel cell (PEMFC) took the spotlight as a promising fuel cell system after 1990, electrocatalyst for ORR research inclined toward the development of carbon supported Pt-alloy catalyst for the application on PEMFC. The first use of Pt-alloy catalyst in PEMFC was reported by the group at Texas A&M University in 1993 [10,11]. They tested the performances of Pt–Cr, Pt–Co, Pt–Ni with 20wt% Pt loading on Vulcan XC72R, a conductive carbon black for catalyst support. These Pt-binary catalysts showed the activity improvement of 20–30 mV over Pt up to current density of 1 A cm^{−2} and the binary catalysts was extended to various transition metals in Jonson Matthey [12]. They also investigated on effect of heat treatment on the stability of the fabricated catalysts and the activity degradation after physicochemical leaching of base metal. Tamizhmani and Capuano further developed the Pt–Cr binary alloy catalyst to the ternary catalyst of Pt–Cr–Cu/C, demonstrating higher mass activity compared to pure single Pt and Pt–Cr binary catalysts [13].

The evaluation of ORR activity of electrocatalysts in aqueous solution allows examination of intrinsic catalyst performance by excluding many practical factors such as mass transfer of reactant, electrode/membrane interface and membrane hydration. Along with the direct application of electrocatalysts to PEMFC system, fundamental researches for evaluation of Pt-alloy catalyst for ORR has been conducted in aqueous electrolyte. Marković et al. reported the dependence of ORR activity on Pt single crystal surface in HClO₄ solutions using hanging-meniscus rotating disk electrodes [14]. Schmidt et al. established thin-film coated rotating disk electrode method for evaluation of ORR activity of Pt/C nanoparticles [15]. Toda et al. conducted basic research on Pt-alloy (Pt–Fe, Pt–Co, Pt–Ni) sputtered on glass substrate for minimizing the poisoning effect by specifically adsorbing anions [16].

Electrochemists and fuel cell engineers started to have an interest in the particle structure of ORR electrocatalysts and catalyst distribution on the electrodes, core–shell electrocatalysts [17] and nanostructured thin-film (NSTF) electrodes [18]. In a core–shell electrocatalyst, Pt shell protects chemical leaching of less-stable non-Pt metals (core) and core metal modifies electronic state and lattice structure of surface Pt atoms to enhance the catalytic performance and selectivity.

The Pt-coated whisker array structure with sub-micrometer thickness, in NSTF possesses a couple of advantages of the catalyst utilization efficiency and the faster introduction of reactant into catalyst/membrane interfaces.

2.1.2. Non-Pt metal catalysts

Although carbon supported Pt-alloy is considered as the best catalyst for ORR at current stage of the technology, it still has four drawbacks [19]:

- (1) Pt is a limited resource and very expensive.
- (2) Pt-catalyzed cathode ORR is not a complete four-electron reaction. Hydrogen peroxide formed through two-electron reaction gives negative effect on the stability of cathode and membrane.
- (3) Pt catalysts are very sensitive to contaminants in the feed system such as NO_x, and SO_x in the air flow. These contaminants cause catalyst poisoning of the active sites, which can be permanent at low-temperature operation.
- (4) In a fuel cell using organic molecules directly as a fuel, a Pt cathode catalyst can also accelerate the oxidation of organic molecules which crossed over from the anode, resulting in the occurrence of mixed potential.

Therefore, during the similar period of developing Pt-alloy electrocatalysts, there has been large effort to develop non-Pt electrocatalysts for ORR as alternatives to Pt-alloy catalysts, including perovskite [20], pyrochlore metal oxides [21], chevrephase Ru–Mo chalcogenides [22], and transition metal macrocycles [23].

It has been known that transition metal (i.e., Fe, Co) N₄-macrocyclic compounds (i.e., porphyrins, phthalocyanines, tetraazannulenes) could be used as electrocatalysts for ORR as demonstrated in Jasinski's discovery of the catalytic properties of Co phthalocyanine [23]. However, they showed low chemical stability in acidic conditions. The decomposition either via hydrolysis in the electrolyte, or an attack of the macrocycle rings by peroxide intermediates was found to be the main cause of the poor stability. Attempts to improve both catalytic activity and stability has led to the discovery that heat treatment of transition metal macrocycles (>800 °C) can significantly improve stability and activity [24,25].

The N₄-macrocycle structure can be destroyed at high temperature over 800 °C, and it is unlikely that the origin of ORR activity is the macrocyclic structure [19]. In addition, Gupta et al. showed that heat treatment of the mixture of polyacrylonitrile (PAN) and iron or cobalt salt also results in ORR activity and stability like heat-treated macrocycle compounds [26]. Because PAN is a nitrogen-containing polymer without N₄-macrocycle coordination, it implies that it is possible to form active species simply by heating the nitrogen-containing carbon source. Therefore, a fundamental curiosity occurred among many studies to understand how carbon, nitrogen, and transition metal constitute the active sites for ORR. Lefèvre et al. conducted ToF-SIMS (Time of Flight-Secondary Ion Mass Spectrometry) to identify the active site of the pyrolyzed macrocycle molecules [27]. They reported that there is a correlation between FeN₂C₄⁺ detection and electrochemical ORR activity over 800 °C. It indicates that metal atom bound to nitrogen atoms such as Fe–N₂ or Fe–N₄ is a potential candidate of ORR-active site [27,28].

Nallathambi and coworkers reported on metal-free carbon–nitrogen composite ORR catalysts fabricated by pyrolysis of Co–Fe–N chelate complex and subsequent chemical leaching of metals [29]. They confirmed that metal-leached nitrogen–carbon composite catalyst shows better catalytic performance than the unleached one via RRDE experiment and PEMFC test. Based on the result, they claimed that nitrogen-associated carbon is the active site and metal is not the active site but it just helps nitrogen atoms incorporate into graphite structure to form active sites. In addition, Dai and coworkers reported on the vertical arrays of nitrogen-doped (N-doped) carbon nanotube (CNT) and N-doped graphene as a metal-free electrode with a superior ORR activity, long-term operation stability, and tolerance to fuel crossover effect when it is compared with 20wt% Pt/C in alkaline fuel cells [30,31]. On the other hand, Lefèvre et al. fabricated micro-porous carbon supported Fe-based catalysts showing a comparable performance to Pt in PEMFC at low current density around the same time [32]. Summarizing two different approaches, we can see that there is a controversy about the role of the transition metal in this type of non-Pt ORR catalyst whether it is an active site or it is a promoter of the formation of ORR-active nitrogen–carbon composites.

Regarding this controversy, Liu et al. developed a pyrolyzed nitrogen-containing carbon catalyst without metal even in fabrication process of the catalyst [33]. In addition, there is a numerical simulation result for the explanation of ORR activity of N-doped graphite [34]. Therefore, it seems to be certain that nitrogen-containing carbon is an active material for ORR and metal promoter is not necessary in some cases. Regardless of the role of transition metal in nitrogen–carbon composite catalyst, exclusion of transition metal is desirable in PEMFC application because metallic cations leached from the cathode during the operation

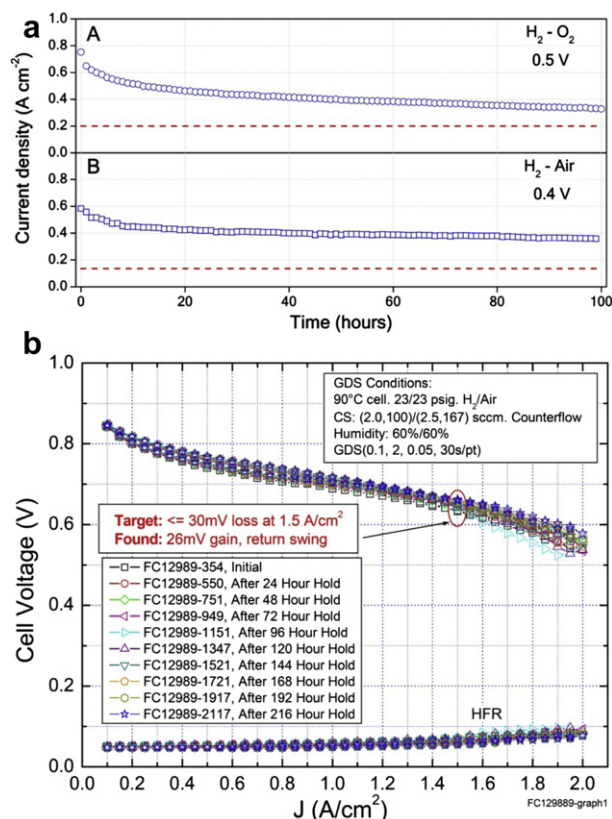


Fig. 5. (a) Current density monitoring to evaluate the durability of Fe-N₄/C catalyst with 5.6 mg cm⁻² loading at 0.5 V of H₂-O₂ fuel cell and 0.4 V of H₂-air fuel cell [32]. The cell temperature is 80 °C, 100% RH, and back pressures of H₂-O₂ are both 30 psig. The red dashed line is the durability test result of Bashyam and Zelenay (reprinted by permission from Macmillan Publishers Ltd: Nature [38], 2006). (b) J-V plot with time at a fixed potential 1.2 V to test the durability of Pt-Co-Mn NSTF catalyst with 0.15 mg-Pt cm⁻² loading (reprinted with permission from [37], Copyright 2008 US DOE). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

degrade the proton conductivity of the membrane due to exchange of hydrogen ions in membrane to metallic cations [35].

2.1.3. Applications of electrodes for oxygen reduction reaction

Although various non-Pt electrocatalysts have been developed for several decades, there is no superior alternative to Pt for the application of low-temperature fuel cells, especially PEMFCs. In particular, non-Pt catalysts never have accomplished similar stability of Pt-alloy in acidic media to date [36].

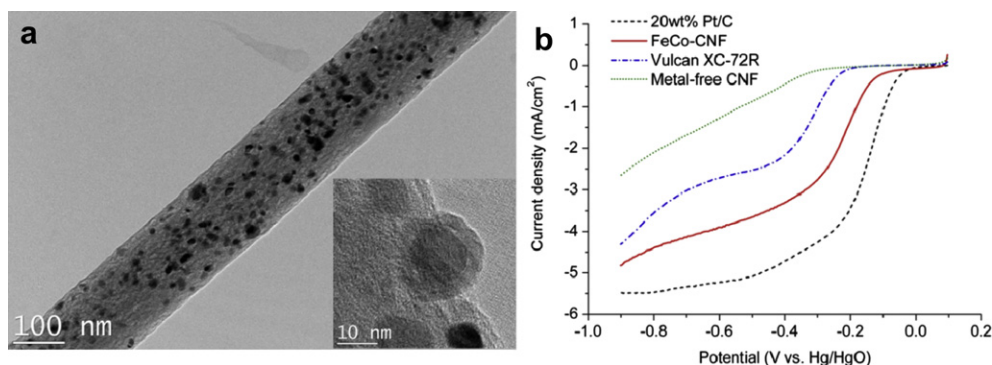


Fig. 6. (a) Iron-cobalt composited carbon nanofibers, (b) electrochemical activity of Fe-Co/CNFs [42].

Herein, we introduced two interesting experimental observations of fuel cells applying non-Pt and Pd based alloy electrodes (see Fig. 5). The durability tests of carbon supported iron-based catalyst and Pt-Co-Mn ternary NSTF catalyst with 0.15 mg-Pt is presented in Fig. 5. These catalysts are considered to be in the best level of performance among their own type of catalysts [32,37]. Although the test conditions and the visualized quantities are different to each other, we can compare the durability of each catalyst by evaluating the fraction of the final power performance over the initial one and by considering whether the test condition is favored or harsh to the catalyst.

The test condition of Pt-Co-Mn catalyst was harsher than that of iron-based catalyst. The potential for the test is 1.2 V, which is a more oxidizing condition to cause chemical leaching of catalysts or support loss by carbon oxidation ($C + O_2 \rightarrow CO_2$), and the test time was twice of the time for the iron-based catalyst. The performance degradation of Pt-Co-Mn NSTF catalyst is not observed even after 200 h operation at 1.2 V while iron-based catalyst showed over 30% performance loss for 100 h operation at 0.4 V, which is the milder condition.

The durability is more crucial requirement of an ORR catalyst for the commercialization of PEMFCs [39], since the cheaper catalyst with less long-term stability can increase the maintenance cost by frequent replacement of degraded catalyst. Therefore, further research is necessary for the improvement in the stability of non-Pt catalysts to be promising alternatives to Pt-alloys in acid media. Pyrolyzed Me-N-C composite catalysts have a potential as an alternative ORR catalyst in alkaline fuel cell (AFC) cathodes due to the lower activating energy for ORR [40]. In addition to N-doped CNT and graphene developed by Dai and coworkers [30,31], Acta A.p.S which specializes in alkaline electrolyzer and fuel cell, developed a commercial non-Pt ORR catalyst based on Me-N-C composite fabricated by their own proprietary method for alkaline ethanol fuel cells [41]. Of late, iron-cobalt modified carbon composite nanofibers have been developed for the purpose of direct electrode fabrication with ORR-active catalytic sites (Fig. 6) [42]. If a solution for the problem of carbonate formation in the electrolyte is provided or a highly performing anion exchange membrane is developed, then AFCs might attain a chance of its Renaissance with the further development of the alternative Me-N-C composite ORR catalysts.

2.2. Oxygen evolution reaction

In 1874, Jules Verne, the science fiction pioneer from France, authored the novel "The Mysterious Island", in which an engineer tried to answer a difficult question on what will humankind use when the natural fuels will be depleted, to which he answered "water, but split into its chemical elements and doubtlessly split by

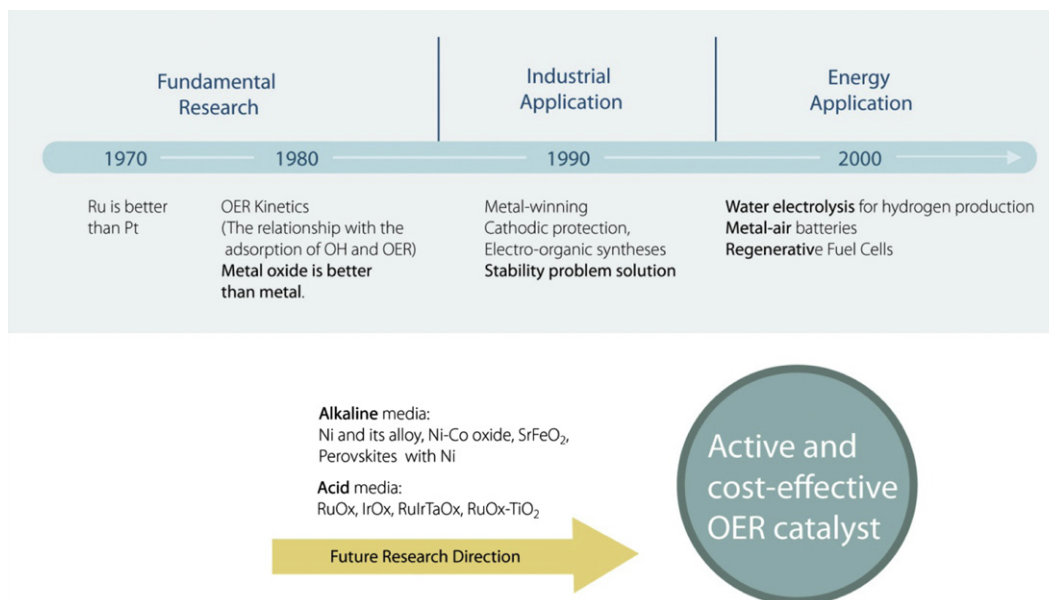


Fig. 7. Brief historical timeline of OER catalyst development and the foreseen shift in research focus to future OER electrocatalysts.

electrolysis" [43]. Since the discovery of the first water-splitting system by Nicholson and Carlyle using Volta's pile, many kinds of materials and derivatives have been discovered as electrocatalysts for this reaction. Early transition metal oxide electrodes for oxygen evolution mostly deal with the chlor-alkali process invented by Beer in 1960's, since active materials for chlorine evolution are also shown to be active for oxygen evolution [44,45]. First developed in Italy, it generally consists of a passive metal support (i.e. titanium) coated with the oxide film of noble metals (RuO₂, IrO₂, TiO₂) [45]. Fig. 7 shows the timeline of the development of OER electrocatalysts from its basic studies to industrial processes to the current targeted use for modern energy conversion and storage devices.

Transition (Ni, Co, Mn) and noble (Ru, Ir) metal oxides have been considered to be the best anode OER materials in alkaline and acid media, respectively, because they cannot be easily further oxidized. Some of the transition metal oxides (i.e. PtO₂, MnO₂, Co₃O₄ and NiO) exhibit semiconducting property, while the others (i.e. RuO₂, IrO₂ and RhO₂) show metallic conductivity. This difference in electronic behavior is believed to be determined by the degree of interaction between the orbitals of the transition metal cation in the lattice and the number of d-electrons [46].

2.2.1. Noble metal oxides

Among noble metal oxides, RuO₂ is the most active but is fairly expensive. The interest in RuO₂ electrodes started due to its reactivity at high current densities in chlor-alkali cells [47,48]. It has metallic-like conductivity in basic and acidic media, but it is slowly attacked by alkaline electrolytes and loses its activity. It is usually prepared through thermal decomposition of metal salts on Ti substrates. Sintered-type with Teflon binder, sputtered film and single crystal RuO₂ electrodes have been utilized for OER, with the single crystal showing the highest Tafel slope depending on the crystal orientation [49–51]. Based on the experimentally observed OER kinetics, several mechanisms have been proposed, one involving the oxidation–reduction cycle mechanism together with dissolution [44,50]. The dissolution of RuO₂ electrocatalysts has been extensively studied and was found to occur even if the electrocatalytic properties are good. Any increase in electrocatalytic activity will lead to a decrease in anodic stability [44]. Similar

studies have been performed to compare Ru metal and RuO₂ stability, it was found that RuO₂/Ti electrodes are corrosion-stable around 1.5–1.8 V vs. SCE [52]. However, it had short life-time due to the formation unstable RuO₄ and subsequent dissolution [53,54].

IrO₂ exhibits the lowest overpotential for OER in acid, but it has poor resistance to corrosion and has slightly lower activity than RuO₂. IrO₂ electrodes are usually prepared through electrolytic growth from Ir precursors, thermal decomposition, and sputtering of thin films [55,56]. Deactivation was reported to occur under long-term polarization and related to the increase in the value of the valence of the Ir cation [57].

One approach to improve the stability and corrosion resistance of RuO₂ is to mix it with other metals (i.e. Pt [58]) and metal oxides (Ta₂O₅ [59], TiO₂ [60], SnO₂ [61], ZrO₂ [62], and Sb₂O₅ [63]) to form mixed oxides. Several studies have used RuO₂ and IrO₂ mixed oxides, and in combination with other transition metals as OER catalysts. It has been established that RuO₂ and IrO₂ mixed oxides showed enhanced stability in solid polymer electrolyte (SPE) water electrolysis cells while RuO₂ and TiO₂ claimed to exhibit synergetic effects [50]. This approach is shown in the study by Mamaca et al. [64], they found that the presence of Ir contributed in the stability against Ru dissolution (Fig. 8).

2.2.2. Non-noble metal oxides

Nickel (Ni) is the most practical OER electrode in alkaline water electrolyzers. Ni and its alloys possess many of the desirable characteristics for practical electrodes for OER. Porous Ni electrodes are usually used both as hydrogen and oxygen electrodes in water electrolytic cells to increase the three phase contact area to achieve high power density and operating current density [65]. They are highly resistant to corrosion and relatively inexpensive. The overpotential for OER on Ni electrodes is higher than desired, but it is reduced by applying electrocatalysts or increasing the effective surface area of the electrode such as in the case of Raney Ni.

Another class of compounds is spinel oxides in terms of activity, availability, low cost, thermodynamic stability, low electrical resistance and environmental friendliness for ORR and OER in alkaline media [66]. There have been a number of number techniques to prepare spinel type oxides at a lower cost but with increased reliability. These techniques include thermal

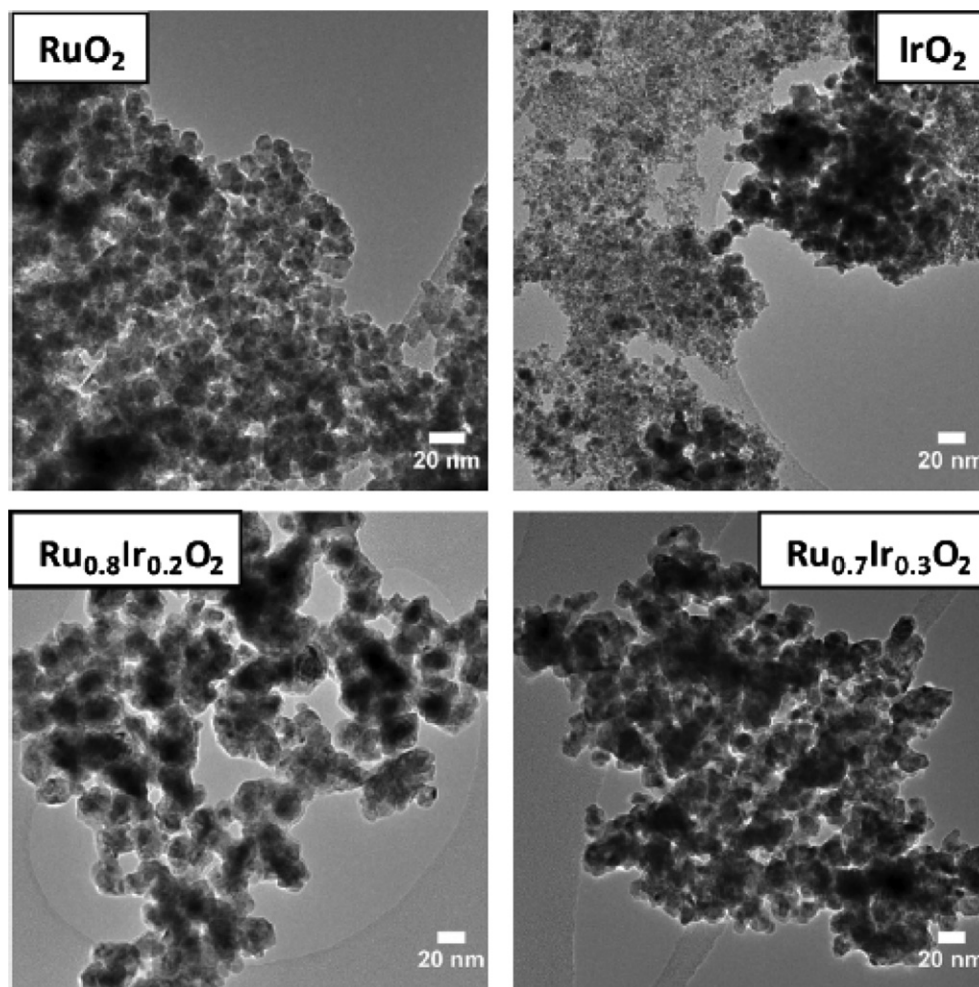


Fig. 8. Transmission electron microscope (TEM) images of commonly studied noble metal-based OER powder catalysts synthesized using thermal decomposition (reprinted from [64], Copyright (2012) with permission from Elsevier).

decomposition [67], spray pyrolysis [68], sol–gel [69], electrostatic spray deposition [70], and precipitation [71]. Aside from spinel oxides, perovskites oxides (ABO_3) have been widely studied, since the crystal lattice can host a variety of transition metal oxides with its ability to distort cubic symmetry structure.

It was reported that for alkaline media, the activity sequence of the non-noble along with noble metal oxides is given by: $\text{RuO}_x > \text{RhO}_x > \text{NiO}_x \sim \text{IrO}_{xx} > \text{PtO}_x > \text{PdO}_x$ at a fixed overpotential [72]. The OER using PbO_2 in acid solutions was also studied and found to be dependent on the structure [73]. Although PbO_2 does not have good electrocatalytic activity relative to RuO_2 and IrO_2 , its high corrosion resistance is useful as an industrial electrode material. MnO_2 mixed with RuO_2 as anode material has also been tested and shown to be commercially useful [74].

2.2.3. Applications of electrodes for oxygen evolution reaction

There have been some inspiring ideas on the development of better oxygen electrocatalysts for OER. One approach involves the use of novel carbon materials as catalyst support, because it can lower operation potential at which carbon corrosion is insignificant. A hybrid material consisting of Co_3O_4 nanoparticles grown on reduced graphene oxide exhibited high catalytic activity in ORR and OER arising from synergetic chemical coupling effects between Co_3O_4 and graphene, as shown in Fig. 9(a) [75]. Another idea entails duplicating natural photosynthesis through the use of biomimetic

oxygen-evolving catalysts and self-healing oxygen-evolving catalysts that operates in benign conditions. In the last few years, the Nocera group at MIT developed self-healing OER catalysts that functions in neutral water and from earth-abundant materials. Their cobalt-phosphate OER electrocatalysts (Fig. 9(b)) are formed in situ during anodic polarization at $\text{pH} = 7$ and 1 atm conditions and retained their stability through the action of phosphate as a self-healing component in the system [76,77]. The design of a water-splitting synthetic center that mimics nature in combination with highly conductive carbon based materials was reported recently also. A polyoxometalate cluster assembly on a conducting bed of multi-walled carbon nanotubes (Fig. 9(c)) showed good anodic current with excellent structural stability and retention of electrocatalytic properties [78]. From an electrocatalysis perspective, researchers must widen their perspective on the types of materials that they can work on. The use of tailored, functionalized and nanostructured old and new materials might bring us closer to the goal of finding active, efficient, and stable OER electrocatalysts.

2.3. Bi-functional catalysts

Bi-functional oxygen electrocatalysts is essential in the development of unitized regenerative fuel cells (URFCs) and rechargeable metal–air batteries. URFCs are integrated energy storage and conversion systems consisting of a fuel cell and a water electrolyzer.

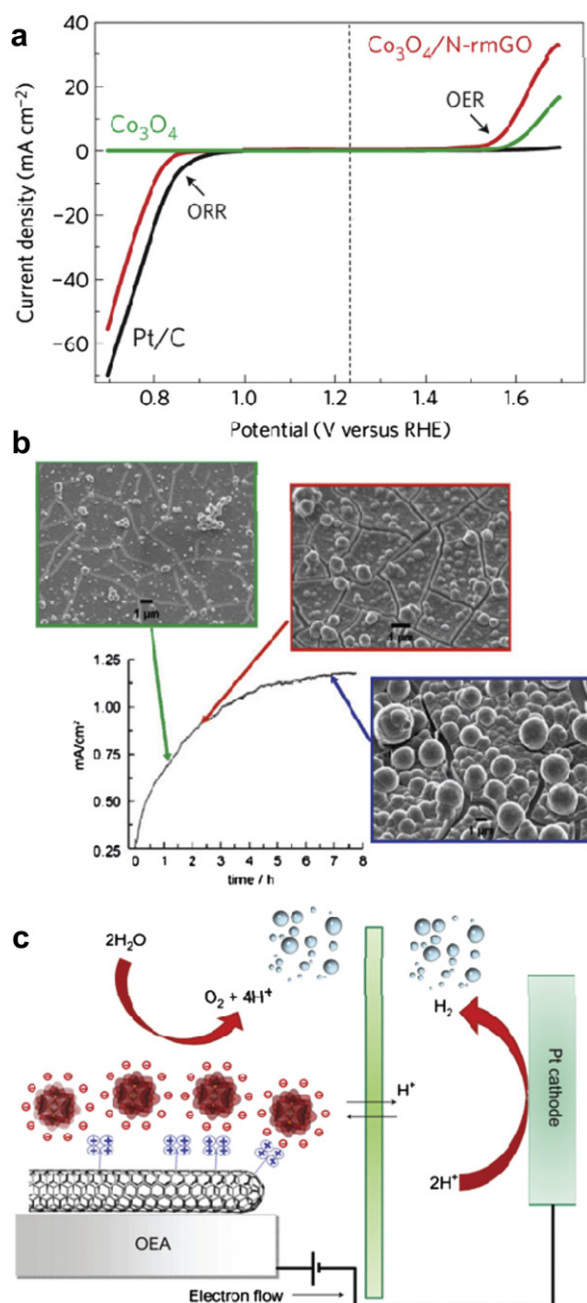


Fig. 9. Some results of recent high-impact studies on OER; (a) Co₃O₄/graphene hybrid bi-functional catalyst activities within ORR and OER potential window in comparison with Co₃O₄ nanocrystals and Pt/C (reprinted by permission from Macmillan Publishers Ltd: Nature Materials [75], 2011), (b) current density profile for the bulk electrolysis at 1.29 V (vs. NHE) in 0.1 M KPi electrolyte at pH 7.0 containing 0.5 mM Co²⁺ with the SEM images of the electrode surface at different time points during the electrodeposition (from [76], Reprinted with permission from AAAS), (c) a general scheme for a water-splitting electrocatalytic cell with the integrated nanostructured oxygen-evolving anodes based on polyanionic ruthenium-containing clusters (reprinted by permission from Macmillan Publishers Ltd: Nature Chemistry [78] 2010).

As a closed-loop system, it can provide high specific energy density and long-term storage option utilizing renewable energy sources (i.e. solar cells, wind turbine, off-grid mini-hydroelectric plants). Aside from the desired high catalytic activity and good electronic property, bi-functional catalysts should be resistant to anodic corrosion and corrosion-resistant to acidic medium [58,79]. To date, it has been reported that the promising bi-functional oxygen

electrocatalysts include several metals (i.e. Pt, Ir, and Ru), metal alloys (i.e. Pt–Ru, Pt–Ir, and Pt–Ru–Ir), metal oxides (i.e. RuO₂ and IrO₂) and their combinations [80,81]. Fig. 10 shows the high dispersion of RuO₂–IrO₂ and Pt particles and the terminal voltage against current density plot at different temperature. In previous studies, the most common approach to obtain highly active bi-functional catalysts is to combine an efficient ORR electrocatalyst (i.e. Pt) with efficient OER electrocatalyst (RuO₂ and IrO₂). Of these composite bi-functional catalysts, recent attempts have been made to increase the specific surface area, enhance the electronic conductivity, lower the ohmic resistance, maintain a long catalytic activity and improve corrosion resistance at high anodic potentials [82,83].

Oxygen electrodes in rechargeable metal–air batteries consume oxygen during electricity generation while oxygen is evolved during battery charging or electrolysis mode [84]. Usually, alkaline electrolytes is employed in metal–air batteries to improve performance of the oxygen electrode and prevent corrosion of the metal electrodes.

2.4. Catalyst design by bridging theory to real catalyst

The prediction of catalytic activity using intrinsic material properties is important in the design of cost-effective and active catalysts for oxygen electrocatalysts. The goal is to find correlations between electrochemical activity and physicochemical properties [1]. One is linear line representing a scaling relationship and the other is a curve with a maximum called *volcano plot* which corroborates the established Sabatier's principle of catalysis, the interactions between the catalyst and the reactant should be neither too strong nor too weak for the best activity. Along with the support of well-defined model surface study using science techniques in ultra-high vacuum condition, numerical computation provides decisive performance descriptors in terms of physicochemical properties of catalysts and it provides fundamental information on reaction pathway in O₂ electrocatalysis.

For example, Norskov et al. reestablished the trends in ORR activity according to the O and the OH binding energy using a numerical calculation based on extensive work using density functional theory (DFT) calculation (Fig. 11(a)) [85]. Norskov group also attempted to expect the stability of candidate catalyst materials through heat of formation as shown in Fig. 11(b) [86]. Stamenkovic et al. investigated on the effect of alloying, alloy structure of nanoparticles on electrocatalytic activity using well-defined model surface study with assistance of theoretical computation [87].

In addition, based on the information of O₂ adsorption on Pt surface and thermodynamical energy, a model of reaction steps in O₂ electrocatalysis and identification of rate determining step becomes available. For example, Zinola et al. studied on stable configuration of O₂ adsorption on Pt(111), Pt(110) using semi-empirical quantum physical interpretation [88]. They reported that bridge side-on configuration is the most stable coordination geometry, and dissociative O₂ adsorption is favored on Pt(111) implying that four-electron transfer process of ORR to H₂O is more favorable on Pt(111) than Pt(110). In addition, Zambelli et al. conducted direct observation of O₂ dissociation on single crystal Pt surfaces via STM observation [89]. Bocquet et al. simulated the STM images of adsorbed O₂ on Pt(111) with DFT calculation and compared the simulated images with experimental images for O₂ adsorption on bridge site and fcc hollow site of Pt(111) [90].

In OER research, Trasatti first attempted a unified approach to electrocatalysis in transition metal oxides. From the proposed criteria of Tseung and Jasem, overpotential was plotted as a function of the enthalpy of transition from lower to a higher oxide for

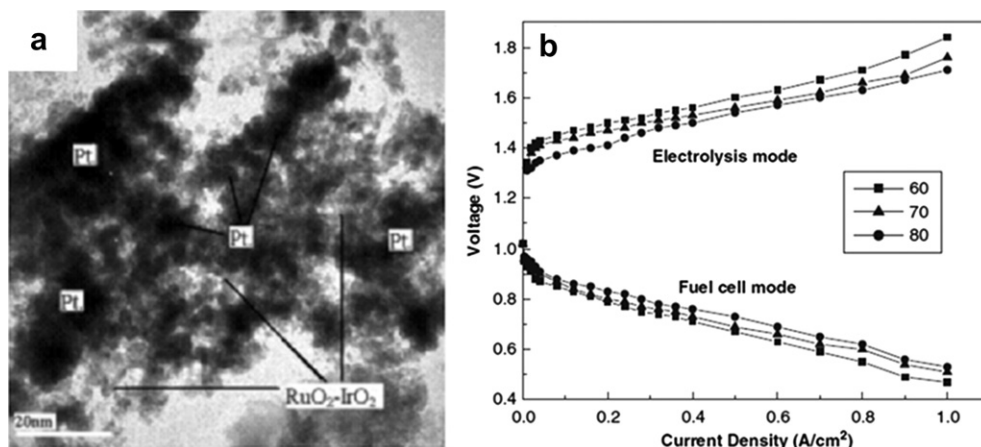


Fig. 10. A bi-functional RuO₂–IrO₂/Pt electrocatalyst for the unitized regenerative fuel cell (URFC) synthesized by colloid deposition, (a) TEM image of the deposited RuO₂–IrO₂/Pt and (b) polarization curves at electrolysis and fuel cell modes (reprinted from [80], Copyright (2007) with permission from Elsevier).

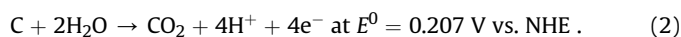
a variety of metal oxides and incidentally RuO₂ was found at the apex of the volcano plot [44,91]. Recently, two major breakthroughs were reported on OER activity descriptors in transition metal oxides using molecular orbital principles and density functional theory (DFT) calculations. Suntivich and coworkers reported a distinct OER activity design principle based on the near-unity occupancy of the e_g orbital of surface transition metal ions and high covalency in bonding to oxygen for the activity of perovskites transition metal oxides [92]. First principles periodic DFT calculations were used to find a universal scaling relationship for a wide range of oxides shown in Fig. 12(b) [93]. Their results indicate that among the materials considered, the OER activity can no longer be significantly improved beyond RuO₂ activity by just changing the binding between intermediate and oxide surface (Fig. 12(a)). The use of three dimensional structures like rough surface structures or co-adsorbate effect on catalyst's surface can enhance preferential stabilization of the desired intermediate in OER.

The electrocatalyst development mainly relied on trial and error experiments based on guessing of the probable material for electrocatalyst. The current theoretical approaches are providing a fundamental answer for the hit we got for optimum electrocatalysts, and furthermore the theoretical prediction combined with the well-defined surface analysis saves unnecessary effort of the exploration for all the possible candidate materials. In the

future, the theoretical expectation approach may develop to level of direct catalyst design on a blue print with the more advanced technologies [53].

2.5. Catalyst support, electrode and other novel approaches

Along with the optimization of catalysts structure, great effort has been invested to improve the catalyst support for uniform dispersion of nanoparticle on the support and longer durability in the oxidative environment of electrochemical cells [94]. Although carbon support has been widely used due to good electrical conductivity, high specific surface area and good chemical stability, it is slowly oxidized to carbon dioxide through long time operation at cathode in fuel cells and at anode in water electrolyzer, which results in long-term performance degradation of electrochemical cells. General electrochemical reaction of carbon corrosion is represented by Eq. (2).



Although carbon corrosion is thermodynamically favorable at the electrode at more anodic electrical potential than 0.2 V vs. NHE, the reaction rate of carbon corrosion is usually very slow. Carbon corrosion causes long-term performance degradation of fuel cells

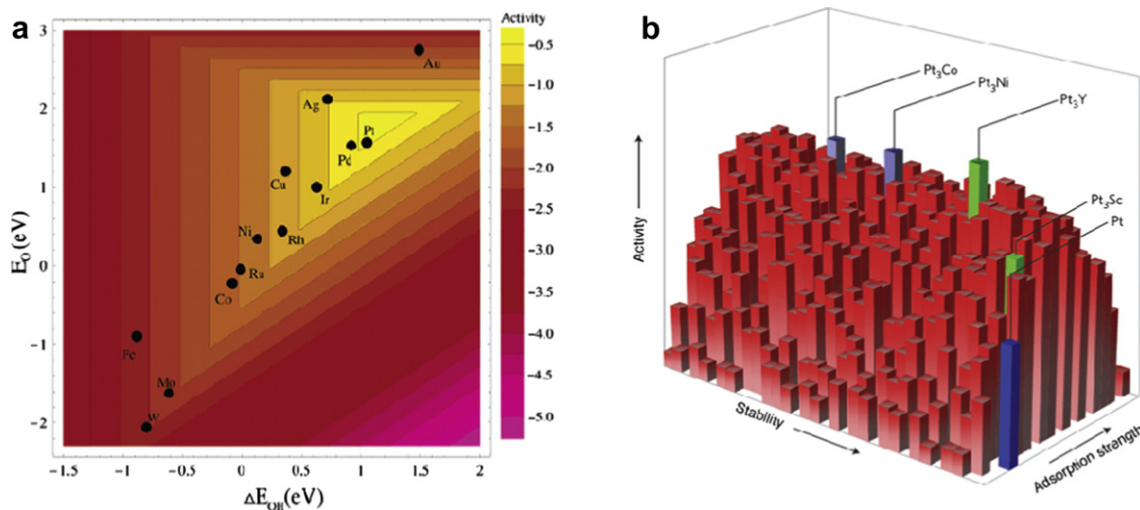


Fig. 11. (a) The expected volcano plot of the ORR catalysts by DFT calculation (reprinted with permission from [85], Copyright 2004 ACS). (b) Trends in ORR activity plotted as a function of both the O and the OH binding energy (reprinted by permission from Macmillan Publishers Ltd: Nature Chemistry [86], 2009).

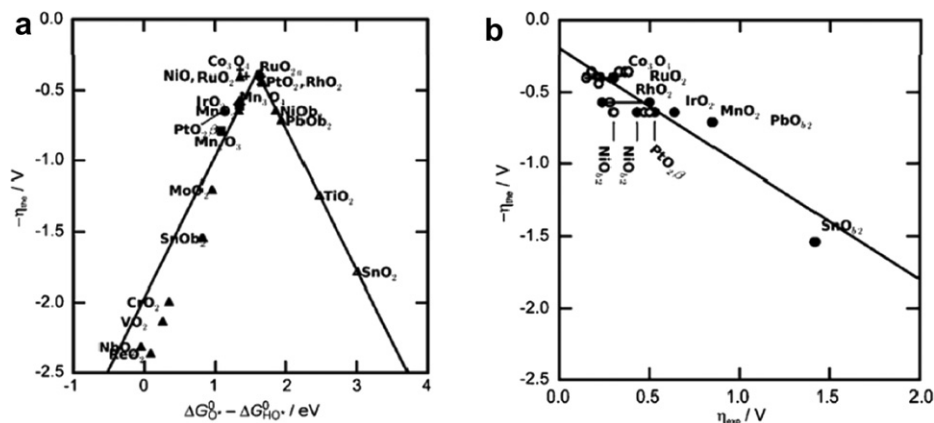


Fig. 12. OER activity trends for rutile, anatase, Co_3O_4 , and Mn_xO_y oxides as (a) volcano plot of theoretical overpotential vs. standard free energy of the step and (b) theoretical overpotential vs. the experimental overpotential in both acidic (●) and alkaline (○) conditions (reprinted with permission from [93], Copyright 2011 John Wiley and Sons).

with the following processes, agglomeration, coalescence, and catalyst loss (Fig. 13(a) and (b)) [95].

Recently, Popov group reported alternative Pt/TiO₂ catalyst for PEMFCs showing excellent stability compared to conventional Pt/C catalyst [95]. Pt/TiO₂ catalyst showed significantly lower degradation after constant potential operation at 1.2 V for 0–200 V as an accelerated durability test whereas Pt/C suffered large degradation due to oxidation of carbon support (Fig. 13(c) and (d)). While they demonstrated improved stability using TiO₂, metal oxides are

usually insulator though some metal oxides are semi-conductor, it is expected that resistance of support can hinder charge transfer from the reaction sites, thereby the electrochemical cell suffers serious ohmic loss. In the case of TiO₂ support, modifying the crystal structure to electrically conductive phase, anatase or rutile can improve the electrical conductivity. In addition, conformal coating of conductive metal oxide like TiO₂ onto the conventional carbon support can provide the protection to the oxidative environment while conserving the electrical conductivity of carbon (Fig. 14(a)).

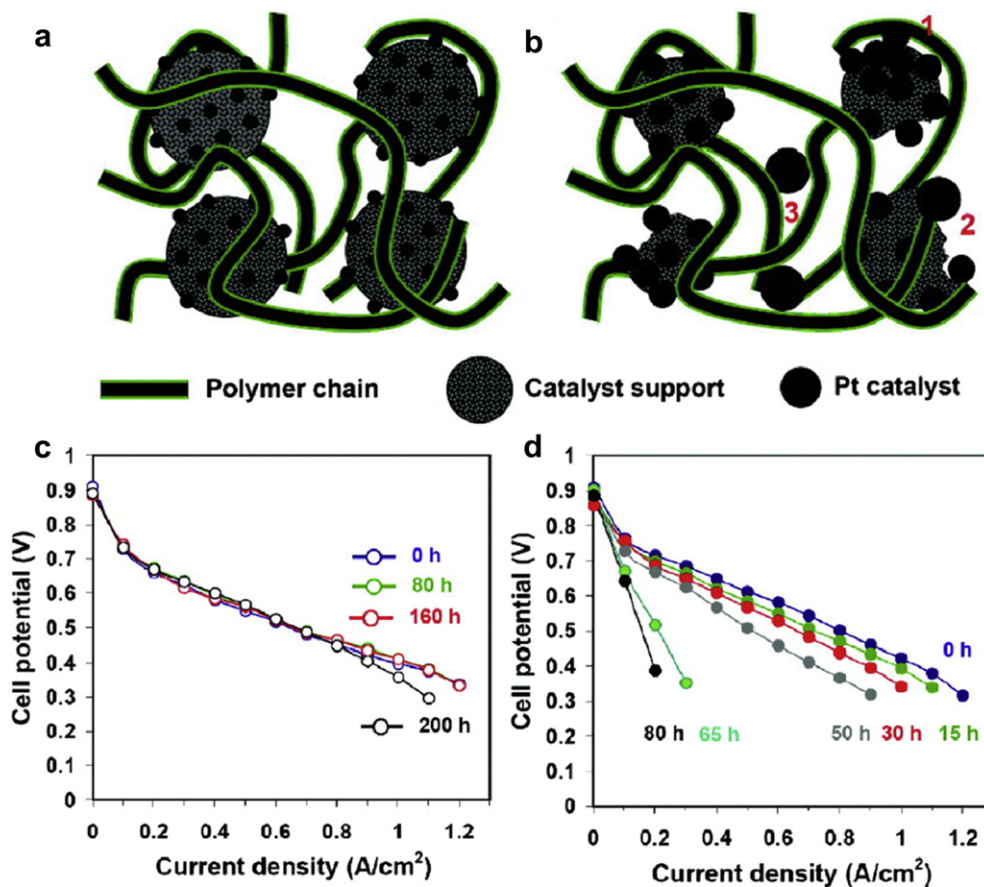


Fig. 13. Schematic representation of the effect of carbon corrosion on (1) agglomeration, (2) coalescence, and (3) loss of Pt particles in the membrane electrode assembly during operation of PEMFCs: (a) normal electrode and (b) corroded electrode. Polarization curves of (c) Pt/TiO₂ and (d) Pt/C after accelerated durability tests (reprinted with permission from [95], Copyright 2009 ACS).

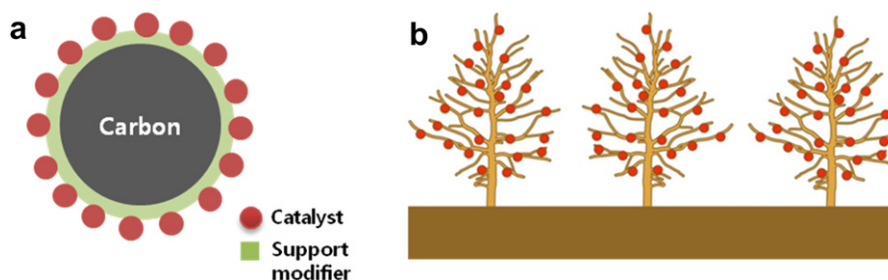


Fig. 14. (a) Diagram of carbon support modified with a conformal coating to reinforce the stability and enhance the catalyst loading distribution and (b) an imaginary drawing of electrode with tree structure.

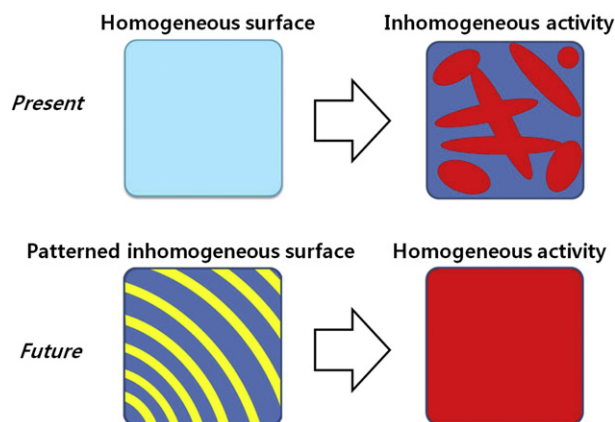


Fig. 15. Schematic diagram of a patterned inhomogeneous surface for homogeneous activity for oxygen electrochemical reactions [98].

NSTF electrodes with a structure look like villi are made of polymer. It also demonstrated superior activity and stability compared to conventional carbon black supported Pt catalysts. Polymeric support enables to make various forms of support structures such as dendrite (Fig. 14(b)) due to its flexible and elastic material properties. Furthermore, there are reports on electrically conductive polymers as a catalyst support. In particular, cobalt–polypyrrole catalyst is a composite catalyst in which cobalt and polypyrrole are associated via chemical bonding rather than Co catalyst supported on polypyrrole [38]. In that case, support–catalyst interaction makes a synergistic effect on catalyst performance in a similar way of interaction between Co_3O_4 catalyst and N-doped graphene support researched by Hongjie Dai and coworkers [75].

Making more durable catalyst is a good idea, but making an eternal catalyst is a better idea. The abovementioned study of Nocera et al. published about self-repairing cobalt oxide thin-film catalyst for OER in aqueous solution containing cobalt ion, phosphate buffer solution [76]. Cobalt thin film is formed on indium-tin-oxide (ITO) glass by anodic electrodeposition during oxygen is evolving on the electrode. The anodic current derived from OER increases along with time in the operation at a constant potential whereas the current usually decreases with respect to time without the self-repair mechanism (Fig. 9). If this self-healing mechanism is generally applied to other catalyst systems, it will be a breakthrough in durability improvement.

Another novel approach that we propose in this review is a patterned inhomogeneous electrode surface. Electrochemical reaction on plain electrode shows inhomogeneous spatial distribution in some cases [96]. It means that it is not necessary to use the same amount of catalyst all over the surface in engineer's point of view. Distributing catalyst on the electrode with an

inhomogeneous pattern surface can induce homogeneous activity distribution over the electrode surface with smaller amount of catalyst (Fig. 15). The idea of electrode with inhomogeneous distribution of catalytic activity can be realized with segmented cells with different catalyst loading amount [97].

3. Concluding remarks

There have been great achievements in reducing the amount of noble metal catalysts to meet the cost-effectiveness criterion including introduction of carbon support, alloying with transition metals, use of structured alloy catalysts and novel design of supports. In non-noble metal catalysts, nitrogen–carbon composites catalysts showed a potential as an alternative to the Pt-based catalysts for ORR in alkaline media and it also shows enhanced OER activity when this composite material is used as a support for loading of a transition metal oxide catalyst like cobalt. However, insufficient durability remains a significant obstacle to overcome in both types of catalysts. In terms of durability issue, chemically more stable support materials such as TiO_2 and the concept of self-healing catalysts are promising solutions to improve the durability. Numerical calculation has been a powerful tool to explain the relation between physicochemical properties and electrochemical activities of catalyst materials. This theoretical approach and the following confirmation through surface science technique will be able to offer an optimum design of catalyst for a specific purpose. In comparison to researches on the components of electrochemical cells such as electrocatalysts, electrolyte, current collecting plate, the research for understanding the interface of catalyst/electrolyte/reactant in O_2 electrochemistry is not yet enough. The idiom “The whole is more than sum of its parts” points this aspect in O_2 electrochemistry. Therefore, we expect that more active interdisciplinary collaboration is essential in the near future to solve the old and challenging problems in O_2 electrochemistry.

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