`Review`

Water Oxidation Mechanism for 3d Transition Metal Oxide Catalysts under Neutral Condition

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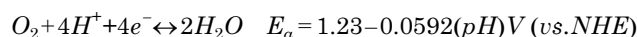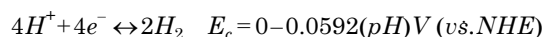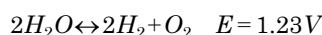
ABSTRACT

Electrochemical water splitting to produce hydrogen energy is regarded as a promising energy conversion process for its environmentally friendly nature. To improve cell efficiency, the development of efficient water oxidation catalysts is essentially demanded. For several decades, 3d transition metal oxides have been intensively investigated for their high activity, good durability and low-cost. This review covers i) recent progress on 3d transition metal oxide electrocatalysts and ii) the reaction mechanism of oxygen evolving catalysis, specifically focused on the proposed pathways for the O-O bond formation step.

Key words : Transition metal oxides, Electrodes, Water oxidation, Electrocatalyst, O-O bond formation

1. Introduction

Recently, research on environment-friendly and renewable energy sources to replace fossil fuels are ongoing and active. Various alternative energies such as solar, wind and tidal energies have been proposed but undesirable required operating conditions limits their practical application. Hydrogen energy, on the other hand, can be stably produced regardless of external condition and is easy to store in the form of hydrogen gas. Furthermore, hydrogen possesses high energy density (~142 kJ/g) compared to oil (46 kJ/g) and natural gas (47.2 kJ/g). In this regard, it is attracting attention as a future alternative energy resource. Recently, the department of Energy (DOE) in the U.S. proposed three targets, including targets for hydrogen production, transfer and storage; the DOE target for 2020 of 44.7 kWh of energy consumption for 1 kg of hydrogen production through water electrolysis.

Currently, most hydrogen gas is produced through the gas reforming process, which unavoidably yields CO and CO_2 by-products. Electrochemical water splitting, which operates the reaction with external potential bias, has recently come to be considered as a beneficial and environmentally friendly method, because it does not produce any greenhouse gas.[1,2] Detailed reaction equations can be described in following half-cell reactions.

$$2H_2O \leftrightarrow 2H_2 + O_2 \quad E = 1.23V$$

$$4H^+ + 4e^- \leftrightarrow 2H_2 \quad E_c = 0 - 0.0592(pH)V \, (vs.NHE)$$

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \quad E_a = 1.23 - 0.0592(pH)V \, (vs.NHE)$$

The hydrogen evolution reaction (HER) proceeds at the cathodic side, while the oxygen evolution reaction (OER) happens at the anodic side. Thermodynamically, 1.23 V vs. RHE is needed to initiate the water splitting reaction. Unfortunately, practically, a potential higher than 1.23 V is required and that additional potential is defined as the overpotential.

Moreover, when considering the generation of an additional resistance factor (R_s) by electric conductivity and ion mobility, the overall overpotential required for water electrolysis can be expressed as in the equation below.

$$\eta_{tot} = \eta_c + \eta_a + iR_s \quad (i = i_c + i_c)$$

Therefore, the fundamental issue is to decrease the total overpotential value in the electrolysis system. Engineering issues such as type of working electrode, electrolysis cell configuration and mass transfer are important tasks to be optimized (Fig. 1). Above all, the crucial thing is to develop efficient catalytic materials for each half-cell reaction.

Water oxidation, due to its slow kinetics, is a bottleneck for the overall water oxidation process.[3-5] In the water oxidation reaction, 4 electrons and 4 protons are required in multi-step processes and the formation of single O-O bond is thermodynamically difficult. Therefore, the value of the overpotential for water oxidation is generally much higher than that of HER.

In this regard, substantial efforts have been devoted to the discovery of efficient OER catalysts. For instance, precious metal-based catalysts, such as those based on Ir and

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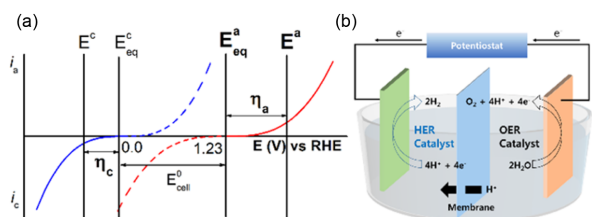 Tel : +82-2-880-7094   Fax : +82-2-880-7094

Fig. 1. (a) I-V curve for the overall water splitting reaction (b) Electrochemical system for water splitting.

Ru, have been studied for their superior activity.[6-8] However, the scarcity and high price of these materials remain as critical barriers. From this point of view, 3d transition metal oxides are promising materials due to their earth-abundant nature and robust stability. Particularly, various Mn, Co and Ni oxide electrocatalysts have been developed, whereas Cu and Fe oxide catalysts have been only rarely reported.

In this review, we cover recent progress in 3d transition metal oxide OER catalysts. Representative discoveries of each catalyst and an activity comparison are introduced. Moreover, we will further focus on the water oxidation mechanism in heterogeneous catalysts. Specifically, proposed pathways for the formation of O-O bond are summarized. Recent studies on two hypotheses, the acid-base (AB) mechanism and the radical-coupling (RC) mechanism are described in detail.

2. 3d-Transition Metal Oxide Water Oxidation Electrocatalysts

First row 3d transition metal-based catalysts have been actively researched in terms of the oxygen evolution reaction. Active research has been done in fields of Mn, Ni and Co based catalysts, while only few studies have been performed for Fe and Cu based catalysts (Fig. 2). Electrochemical measurements of all of the catalysts that we will discuss below proceeded in neutral conditions.

2.1. Manganese based electrocatalysts
Various research groups have developed manganese based electrocatalysts with mixed valency; these electrocatalysts exhibit superior performance. Driess's group developed amorphous MnO_X nanoparticles using ceric ammonium nitrate (CAN) as a chemical oxidant (Fig. 3(a)).[9] The amorphous MnO_X compound was found to have higher activity than that of inactive crystalline MnO nanoparticles. The researchers proposed that the improved catalytic activity in amorphous MnO_X could be attributed to the change of the average oxidation state from 2.0 to 2.5 via CAN treatment.

Mn oxide catalysts with mixed valency were also synthesized by electrodeposition method. Dau's group developed MnO_x catalysts via electrodeposition and estimated the average oxidation state of Mn (Fig. 3(b)).[10] The values of the oxidation state in active and inactive MnO_x films were 3.8 and 4.0, respectively. In Nocera's group, electrodeposited manganese oxide films (MnO_X) were proposed as promising stable catalysts for water oxidation at neutral pH (Fig. 3(c)).[11] They revealed two competing pathways under neutral pH, a one-proton coupled one-electron transfer (PCET) process and an Mn(III) disproportionation reaction. Additionally, Kuo's group reported mesoporous MnO_X with high surface area fabricated via a single-step soft-templated wet-chemistry approach (Fig. 3(e)).[12]

Nakamura's group synthesized MnO_2 nanoparticles and detected reaction intermediates by *in-situ* UV-vis spectroscopy.[13] Spectra related to Mn(III) species were observed with an accompanying increase of the catalytic current density. It was revealed that Mn(III), which is inherently unstable at neutral pH due to the disproportionation reaction, served as the precursor of the catalysis. Furthermore, in subsequent research, the group generated N-Mn bonds on the surface of MnO_2 via a ligand exchange with poly-(allylamine hydrochloride) (PAH).[14] The N-Mn bonds restricted the disproportionation process and stabilized the Mn(III) under neutral pH. Therefore, the effect of the ligand exchange method decreased the onset potential by ~500 mV for the MnO_2 catalysts.

Nam's group developed $Mn_3(PO_4)_2$-$3H_2O$ with asymmetric geometry and found that it had superior efficiency.[15] Also, after synthesizing various catalysts with different Mn oxidation states by extracting Li atom from as-synthesized $LiMnP_2O_7$, they found enhanced water-splitting perfor-
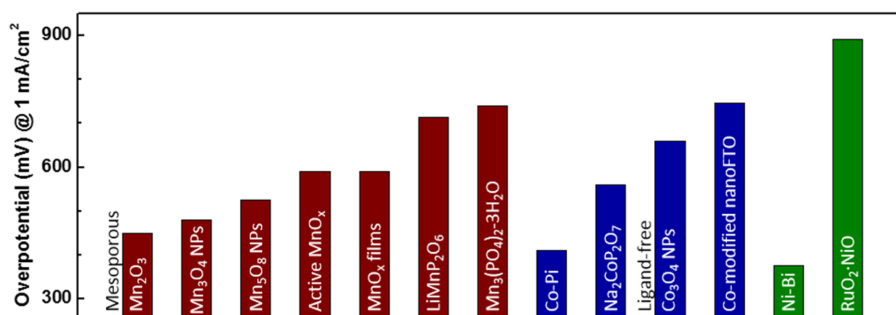

Fig. 2. Overpotentials of various Mn-, Co- and Ni-based electrocatalysts at 1 mA/cm². Activity for the Mn-(wine) and Co-(blue) based electrocatalysts are measured under neutral condition, while nickel borate(Ni-Bi) and $RuO_2 \cdot NiO$ are operated at pH 8.5 and 5.5, respectively.
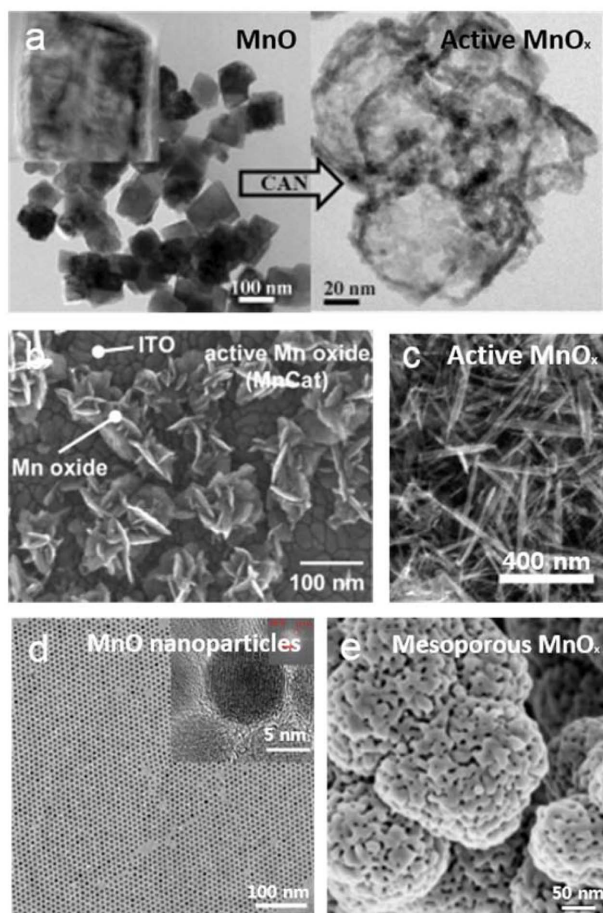
Fig. 3. Morphology of representative Mn-based electro-catalysts. (a) inactive crystalline MnO (left) and active amorphous MnO_x (right) after partial oxidation by ceric ammonium nitrate (CAN), (b) electrodeposited MnO_x active catalysts, (c) activated MnO_x catalysts, (d) mono-dispersed 10 nm-sized MnO nano-catalysts synthesized by hot-injection method and (e) mesoporous MnO_x synthesized by soft-templated method.

mance as the Mn oxidation states increased.[16] Recently, they further developed partially oxidized monodisperse 10 nm MnO nanoparticles by conventional hot-injection method (Fig. 3(d)).[17] Furthermore, they synthesized Mn-based oxide nanoparticles with various phases such as Mn_5O_8 and found that the water-splitting efficiency of nano-sized manganese oxide nanoparticles was superior to that of bulk-sized manganese oxides.[18]

2.2. Cobalt based electrocatalysts

Cobalt based electrocatalysts for water oxidation have been largely reported in company with manganese based ones. A notable cobalt based electrocatalyst is cobalt phosphate(Co-Pi), reported by the Nocera group; it was found that this material could be easily deposited on indium tin oxide (ITO) or other inert anodes by anodic polarization in neutral Co(II) containing phosphate solution.[19] The group determined that an amorphous cobalt oxide film was formed
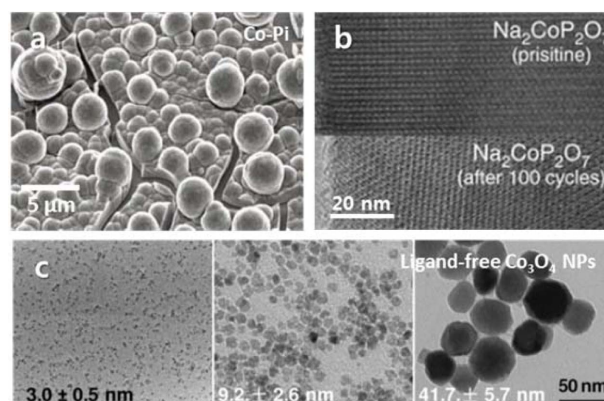

Fig. 4. Morphology of representative Co-based electro-catalysts. (a) Cobalt phosphate catalysts electrodeposited on indium tin oxide electrode, (b) surface region of $Na_2CoP_2O_7$ before and after catalysis and (c) ligand-free Co_3O_4 nanoparticles with various sizes noted in each images.

during electrodeposition in a neutral phosphate solution (Fig. 4(a)); its oxygen evolving performance under such mild conditions was highly active, with almost 100% Faradaic efficiency. Furthermore, Co-Pi was found to be able to sustainably catalyze the water oxidation reaction through the self-repair process, in which the in situ formation of Co-Pi occurred during catalysis in Co(II) containing phosphate solution at pH 7.

Of relevance to the Co-Pi material, Nam's group reported $Na_2CoP_2O_7$ with high catalytic activity and phase stability in 0.5 M sodium phosphate buffer at pH 7; this material was different from the conventional cobalt based electrocatalysts in terms of its local structure of cobalt and a water oxidizing mechanism including a dissimilar rate determining step (Fig. 4(b)).[20] In contrast with the five- and six-coordinated octahedral Co-Pi with stabilized Co(III)/Co(IV) valence states, $Na_2CoP_2O_7$ has a four- and five-coordinated tetrahedral structure with stabilized Co(II)/Co(III) valence states, which enables a minimization of the theoretical overpotential for water oxidation.[21,22] This work suggested that the catalytic activity for OER could be enhanced by tuning the atomic geometry of metal oxides.

Nanostructured cobalt oxides have also been suggested as water oxidizing electrocatalysts that can show improved electrochemical properties compared with those of conventional bulk cobalt oxides.[23-25] A representative example is the ligand-free Co_3O_4 nanoparticles reported by Wang's group in 2013.[23] They synthesized and compared various spinel-type Co_3O_4 nanoparticles with different sizes (Fig. 4(c)) and concluded that the catalytic properties in neutral 0.1 M potassium phosphate electrolyte could be enhanced by minimizing the particle size to increase the surface area available for water oxidation.

In addition, Meyer's group introduced cobalt-modified fluorine-doped tin oxide (FTO) to water oxidation catalysis in 0.1 M phosphate with 0.5 M added $NaClO_4$ at pH 7.2.[26]

They suggested that, with deprotonation, the surface-bound Co(II) species would be oxidized to Co(III) and successively participate in water oxidation catalysis; this process could be maximized by increasing the surface area of the FTO substrate.

2.3. Nickel based electrocatalysts

Rresearch on Ni-based catalyst for water oxidation was started by Bode in 1966.[27] Research on Ni-based catalysts has been primarily done in alkaline conditions, but there are some experiments that have implemented neutral conditions; we will discuss those experiments below.

Juodkazis's group thermally deposited RuO_2 and NiO oxides on a titanium electrode and found that, in a neutral solution of K_2SO_4 (pH = 5.5), the oxygen evolution process was significantly hindered.[28] In their subsequent research, nickel surface anodic oxidation was implemented prior to the oxygen evolution reaction and the changes in the surface state of the nickel electrode in acid, neutral and alkaline solutions were investigated and found to show the beginnings of an oxygen evolution reaction at ~2.0 V (vs. RHE) in neutral medium (pH = 5.5).[29]

Nocera's group electrodeposited a nickel-borate catalyst from dilute Ni^{2+} solution in a borate electrolyte at pH 9.2.[30] In further research, they performed Tafel analysis in various pH conditions ranging from pH 8.5~14; their calculated Tafel slope was 32 mV/decade in well-buffered electrolytes at pH 8.5.[31]

2.4. Iron and Copper based electrocatalysts

While Mn, Ni and Co based heterogeneous electrocatalysts have been suggested for their great oxygen evolving activity and stability under neutral conditions, iron or copper based electrocatalysts have only rarely been studied. Rather, iron or copper has been reported as an active metal site in molecular catalysts for water oxidation, in the following examples: Masaoka's group designed a pentanuclear iron catalyst with great efficiency and redox flexibility.[32] They confirmed six different oxidation states of the pentanuclear iron complex and defined an active state for water oxidation, the $Fe(III)_5$ state. In the case of copper based molecular catalysts, Meyer's group investigated a copper(II) polypeptide complex, the triglycylglycine macrocyclic ligand (TGG^{4-}) complex of Cu(II), for efficient water oxidation.[33] They suggested a water oxidation mechanism of the copper-cored polypeptide complex, in which activated Co(IV) species would oxidize water and release dioxygen with high stability and turnover frequency.

3. Water oxidation mechanism

The water oxidation reaction is a 4-electron, 4-proton process; O-O bond formation is known to be the key chemical step that determines the rate of the whole water oxidation reaction. To develop a catalyst for the water oxidation reaction based on earth-abundant 3d transition metal oxides,

many material factors were controlled such as the composition, phase, morphology and surface structure. However, the precise roles of each component and factor influencing the performance are still not clear. As a result, understanding the reaction mechanism is very important and necessary to rationally design catalysts having superior activity, stability and selectivity.

Investigation of the rate-determining step (RDS) and of the reaction intermediates is thus important to understand the reaction mechanism. Two mechanisms are proposed for O-O bond formation, which is the RDS in the water oxidation reaction. (Fig. 5) The acid (electrophilic)-base (nucleophilic) (AB) mechanism proposed by the Shannon and Frei groups explains that octahedral metal-oxo sites act as mononuclear active sites. Because these metal-oxo sites are considered to be electrophilic, a nucleophilic attack of water molecules naturally occurs to generate peroxo intermediates. On the other hand, the radical coupling (RC) mechanism was proposed by the Najafpour and Voorhis groups. They predicted that the di-nuclear O-O bond formation by adjacent metal-oxo species was the energetically favorable reaction route. Here, we introduce and summarize recent studies on the reaction mechanism for water oxidation catalyzed by 3d transition metal oxides.

3.1. Acid-Base mechanism

For earth-abundant metal-oxide catalysts, Shannon's group proposed a mechanism of cobalt-catalyzed water oxidation in aqueous buffering electrolytes in a pH range of 0-14.[22] Through combined electrokinetic, cyclic voltammetry and electron paramagnetic resonance (EPR) spectroscopic studies, they concluded that Co(IV)-oxo species are crucial intermediates for O-O bond formation. Cobalt metal has mixed valency, with +3/+4 states present in the resting state; Co(IV)-oxo species were generated before RDS. Water molecules react with this Co(IV)-oxo intermediate to generate the O-O bond. The researchers excluded the possibility of a reaction with lattice oxygen atoms because no oxygen gas evolved in the absence of water.[34,35]

To compare the relative stability and activity of various layered cobalt oxide phases, the Bell group performed computational calculations using density functional theory.[21] They found that ß- CoOOH is the active phase, in which the OER occurs in an alkaline environment and the catalytic activity can be attributed to the high valence of Co metal(3+/4+) during the OER. The AB mechanism was used to explain O-O bond formation, because the thermodynamic energy barrier for surface oxygen coupling is almost always larger than associative reaction.[36]

Mechanisms of the other 3d transition metal based catalysts are also reported. For example, Nocera's group studied the water oxidation mechanism of electrodeposited manganese oxide (MnO_x).[37] Through electrokinetic study over a wide pH range, they suggested two competing mechanisms. A one-electron one-proton pair is removed from the surface of manganese oxide via proton coupled electron transfer
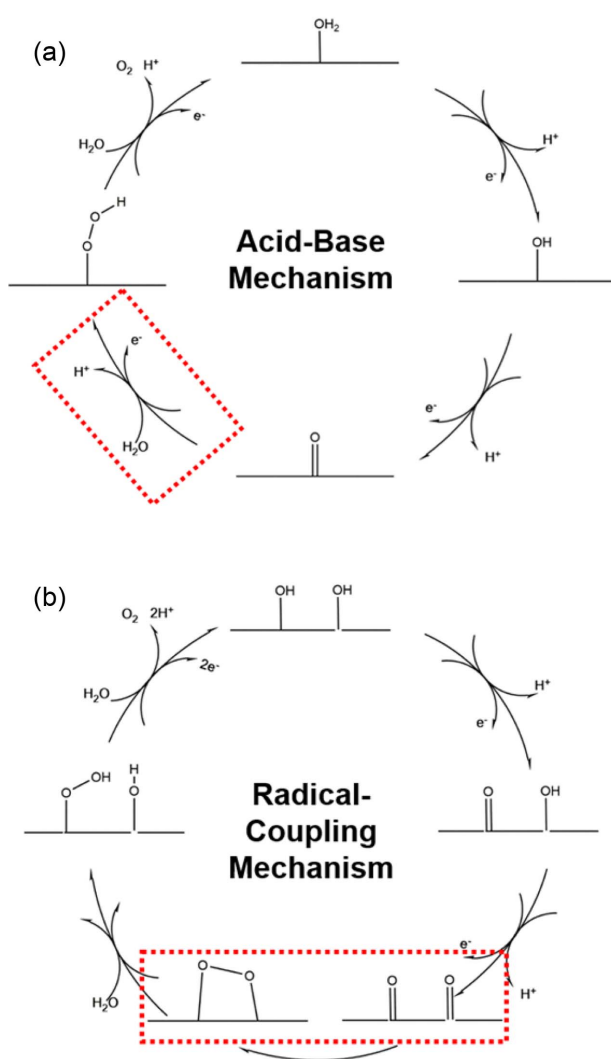
(a)

(b)

Fig. 5. Schematic representation of water oxidation mechanism (a) Acid-Base (AB) mechanism for O-O bond formation (b) Radical-Coupling (RC) mechanism for O-O bond formation.

(a)

(b)

Fig. 6. Schematic representation of Acid-Base mechanism for water oxidation reaction. Proposed mechanisms of (a) partially oxidized manganese oxide nanoparticles at neutral pH by Nam's group and (b) cobalt oxide nanoparticles (Co_3O_4) by Frei's group.

(PCET), which is dominant under alkaline conditions; Mn^{3+} disproportionation mainly occurs under acidic conditions. Finally, Mn(IV) = O sites were generated and O_2 molecules evolved from those terminal oxo sites. Very recently, Nam's group performed in-situ spectroscopic and electrokinetic analyses to reveal the mechanism of partially-oxidized manganese oxide nanoparticles, which were shown to exhibit a superior OER property at neutral pH (Fig. 6(a)). They found that the partially oxidized manganese oxide nanoparticle system shows different mechanistic behavior; the generation of Mn^{3+} is no longer the RDS for the water oxidation reaction. The Mn(IV) = O species were generated as reaction intermediates and O_2 was generated from these oxo sites through the AB mechanism.

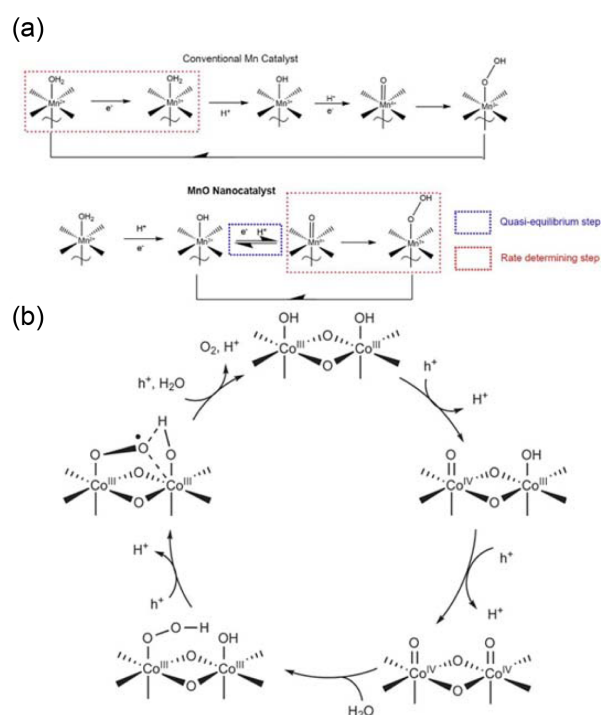Indeed, the AB mechanism from high-valent metal-oxo species has been commonly suggested, especially as the water oxidation mechanism of heterogeneous 3d transition metal oxide catalysts. Recently, important reaction intermediates were characterized by Frei's group.[38] They performed time-resolved Fourier-transform infrared (FT-IR) spectroscopy to identify stepwise cobalt intermediate structures in the catalysis. Two surface intermediates of Co_3O_4 were observed by rapid-scan FT-IR spectroscopy with ^{18}O isotope labeling experiment. A surface superoxide intermediate and Co(IV) = O were detected for the fast catalytic site and slow catalytic site, respectively (Fig. 6(b)). Observation of a surface superoxide intermediate (three-electron oxidation intermediate) would be another important piece of evidence of the proposed mechanism of cobalt oxide. One structural difference between the two intermediates is the nature of the coupling among adjacent Co(III)-OH groups via oxygen bridges, which results in a huge catalytic activity difference.

3.2. Radical-Coupling mechanism

The RC mechanism is also a feasible pathway to generate O-O bonds during water oxidation. In the RC mechanism, O-O bonding is constructed by coupling of two adjacent M=O species because M=O species are isoelectric structures of radical species (M-O·). Generally, based on spectroscopic evidence, the RC pathway has been proposed for O-O bond formation in molecular complex catalysts. However, it was recently reported that the generation of O-O bonding in inorganic catalysts can also be attributed to coupling of two metal-oxo species.

The Sun group reported Ru- based molecular catalysts that exhibited an unprecedentedly high turnover frequency (TOF) of > 300 s^{-1}.[6] For the molecular catalyst Ru(II)-OH_2, the resting state of the active sites was oxidized to Ru(III)-OH_2 and two consecutive oxidation processes generated a reaction intermediate, Ru(V) = O, via proton coupled electron transfer (PCET). Interestingly, the Ru(V) = O species were dimerized to Ru(IV) peroxo dimer, Ru(IV)-OO-Ru(IV), which was detected by UV-vis spectroscopy. Based on the spectroscopic data, it was concluded that the O-O bond formation had progressed by direct coupling of two Ru(V) = O species. Furthermore, the group suggested that organic ligands facilitated the radical dimerization of the Ru(V)=O active species.

The RC pathway was also proposed for the formation of O-O bonds in 3d transition metal oxide catalysts. Najafpour's group investigated the O-O bond formation mechanism using nano-layered MnO_x catalysts.[39] They estimated the exchange rate of $H_2^{18}O$ for μ-O species (Mn-O-Mn) in MnO_x during catalysis. Spectra from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of the μ-O species did not change during catalysis in $H_2^{18}O$. These results indicate that the oxygen atoms of the μ-O species are not involved in the O-O bond formation. As can be seen in Fig. 7(a), the group suggested that not only the AB mechanism (pathway i) but also the RC mechanism (pathway ii) was feasible in the nano-layered MnO_x.

The Voorhis group theoretically investigated the water oxidizing mechanism of Co-Pi. As shown in Fig. 7(b), two adjacent Co(III)-OH species were oxidized to Co(IV) = O via a proton-coupled oxidation process.[40] Through electrokinetic study, Nocera's group corroborated the proton-coupled oxidation step. The free energy barrier to O-O single bond formation was computed using DFT study. Based on the computation results, direct coupling of Co(IV)=O in the cubane structure was suggested as a more favorable reaction pathway. Additionally, the free energy profile as a function of the O-O bond distance additionally supported the idea that direct coupling occurs spontaneously in cobalt catalysts.

4. Summary

In this review, we have covered recent advances in the development of 3d transition metal oxides for water oxidation electrocatalysts. Mn, Co and Ni oxides have been extensively reported as efficient electrocatalysts under neutral condition, whereas Fe and Cu oxides have been only rarely synthesized. The manganese-based catalysts with mixed valency of Mn(III) and Mn(IV) exhibited moderate activity under neutral condition. For Co and Ni oxide-based electrocatalysts, the Nocera group synthesized Co-Pi and Ni-Bi using the electrodeposition method; the resulting materials show benign efficiency at neutral pH. Moreover, revealing the detailed water oxidation mechanism is a demanding issue. In this review, we have demonstrated two hypotheses
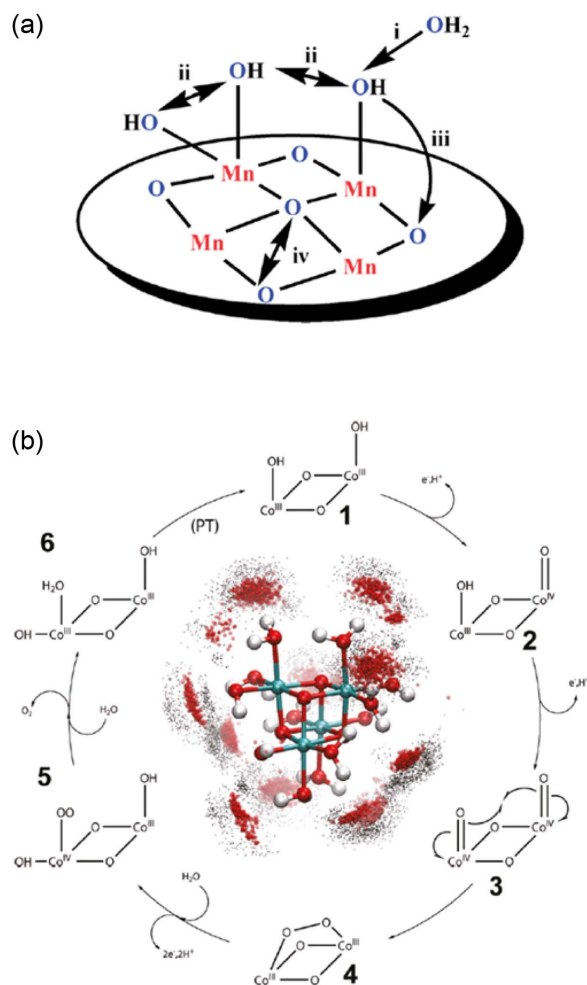

Fig. 7. Schematic representation of radical coupling mechanism for water oxidation reaction. Proposed mechanisms of (a) nanolayered manganese oxide by the Najafpour group and (b) Co-Pi, by the Voorhis group.

(the AB mechanism and the RC mechanism) for O-O bond formation, which is the rate determining step for water oxidation. Generally, O-O bond formation in 3d transition metal oxides has been demonstrated to occur according to the AB mechanism, which generates a single O-O bond via nucleophilic attack. The RC mechanism is generally used to explain the formation of O-O bonds for molecular catalysts. Recently, it was revealed that the RC mechanism had also been suggested for the 3d transition metal oxides. To shed more light on the process of O-O bond formation, more advanced in-situ analysis, such as time-resolved spectroscopic measurement, is required.

Acknowledgments

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