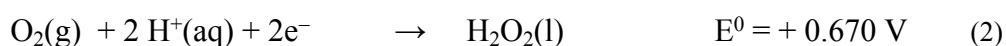
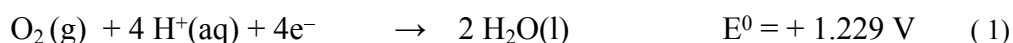


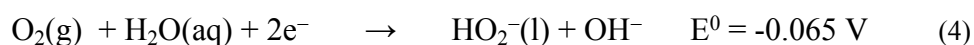
Oxygen Reduction Reaction

Oxygen is the most common oxidant for most fuel cell cathodes simply due to the availability of the oxygen in the atmosphere and the large thermodynamic driving force of the ORR. There are two possible ways of reductions that can take place. Oxygen can reduce to water by direct 4-electron pathway (Equation 1 and 3) or to peroxide by 2 electron pathway (Equation 2 and 4). The most desirable one is the 4-electron pathway.

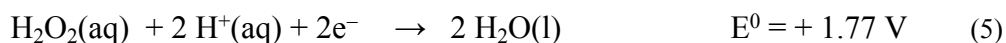
ΔE value of ORR is different at different pH values. Hence, the reaction can be written in different ways according to the medium at which the reaction is taking place. At the acidic medium (at pH = 0, $[H^+_{(aq)}] = 1 \text{ mol dm}^{-3}$) two different pathways of ORR can be written as follows.



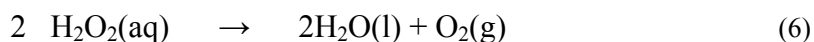
At the alkaline medium (pH=14, $[OH^-_{(aq)}] = 1 \text{ mol dm}^{-3}$) reactions are represented as Equation 3 and 4, respectively.



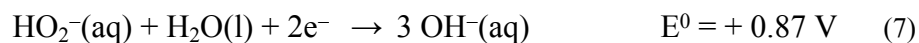
2-electron pathways generate unstable peroxides as products. These species can further reduced to water in the acidic medium.



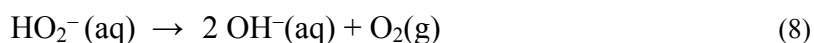
or it decomposes by a disproportionation



The reduction of peroxide can also take place in alkaline media.



or it decomposes



ORR is the slowest reaction in any condition of the fuel cells. There are several reasons associated with this case. One of them is the higher bond energy of the oxygen molecule.



This activation barrier should be overcome to get a higher current density from the cathode. The entropy change (ΔS) of dissociation of O_2 is always positive (increase the randomness). Hence, oxygen dissociation is more favorable at higher temperatures (decrease the ΔG) according to the Equation 10.

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

However, the ΔS for the overall reaction is negative (reactant in gaseous state produce a liquid in the equation 1) hence, $-T\Delta S$ becomes positive. Therefore, at higher temperatures the ΔG increases (negative value of ΔG decreases) so that the efficiency will be reduced. However, at the room temperature the activation energy can drop down by lowering the cathode potential or using suitable electro-catalyst.

Catalysts for ORR

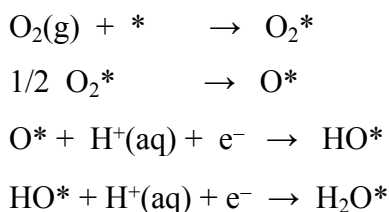
There are different types of ORR electrocatalysts developed in the past 2 decades. However, the following requirements are essential for a good ORR electrocatalyst.

- High catalytic activity towards ORR
- High electrical conductivity
- High chemical and electrochemical stability (should not be oxidized by proton or oxygen or at high electrode potentials)
- Should not dissolve in the electrolyte (insoluble in acidic or basic aqueous solutions or in methanolic solutions)
- Favorable optimum structural composition, favorable morphology, high specific surface area, small particle size, high porosity, and uniform distribution of catalyst particles on the support
- High interaction between the catalyst particle and the support surface
- High catalytic stability (can be affected when one or many of above requirements has/have been failed)

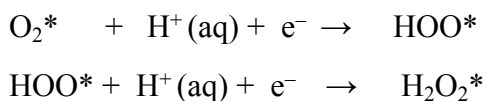
However, there may not be any material that would meet all these requirements at the same time. It can be varied according to the type of the applications and conditions where the catalysts are used .

Transition metals and metal oxides are normally used as catalysts in many purposes. However, the most of them are not shown better catalytic performance towards ORR except few noble metals. The Sabatier principle (introduced by French Chemist Paul Sabatier) is a qualitative concept in chemical catalysis. According to the principle, the interactions between the catalyst and the substrate should not be too strong or too weak. Because too weak interactions lead to failure of making bonds between the catalyst and the substrate, hence no reaction will take place. On the other hand, too strong interactions lead to slow dissociation of the substrate, intermediates or products and then the catalytic surface will not be available for further reaction.

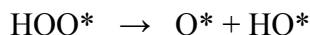
Catalyzed ORR is a multi-step reaction. Therefore, the rate of the rate-determining step is more important than the overall reaction rate. To get a better idea of the Sabatier Principle, the mechanism of the reaction should be known. The basic mechanism of ORR four-electron pathway on a catalytic metal surface can be stated as the following equation sequence.



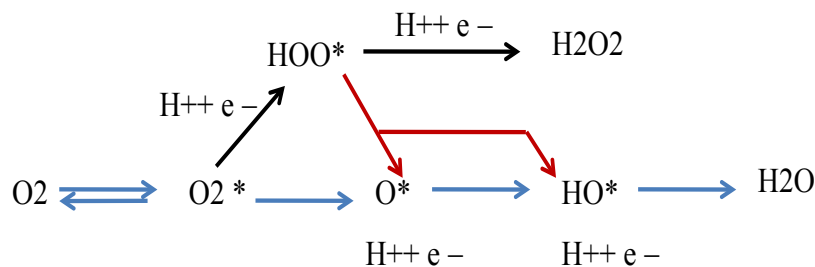
Here * indicates sites on the catalytic surface. Oxygen adsorption is denoted in Equation 1.30 and the O_2 dissociation, OH formation and H_2O formation, respectively, indicate the rest of equations. Water desorption is very fast compared to other reactions and hence the reaction is not mentioned here. For the two-electron pathway, formation of OOH and H_2O_2 takes place as shown in Equation 1.34 and Equation 1.35



Sometimes, OOH^* dissociation can take place at the same catalytic surface as



For overall reaction the following figure summarize the all possible mechanisms.



The summary of the mechanisms of all pathways for ORR

The summary of the mechanisms indicate the four-electron (blue) and two-electron (black) pathways. However, the red colored pathways will affect to vary of the number of electrons transferred from 2 to 4. Then, let's discuss the rate of important steps for different metal catalyst.

1.1.1 Metal Catalysts

Nørskov *et-al* states that the adsorbed oxygen (O_2^*) and hydroxyl (OH^*) are found to be very stable intermediates at the equilibrium potential (+ 1.229 V) for metallic surfaces, and the calculated rate constant for the activated proton/electron transfer to adsorbed oxygen or hydroxyl is related quantitatively for the observed kinetics. Hence, the rate determination step should be Equation 1.31 or Equation 1.33, according to the surface nature effect to E_{OH^*} or $E_{\text{O}_2^*}$. The maximal catalytic activity of some metals towards ORR and the relationship to the binding energies of oxygen and hydroxyl on (111) surfaces are discussed according to the following volcano plots. These plots prove the Sabatier principle as well [J. K. Nørskov *et al J. Phys. Chem.*, **2004**, 108, 17886-17892.]

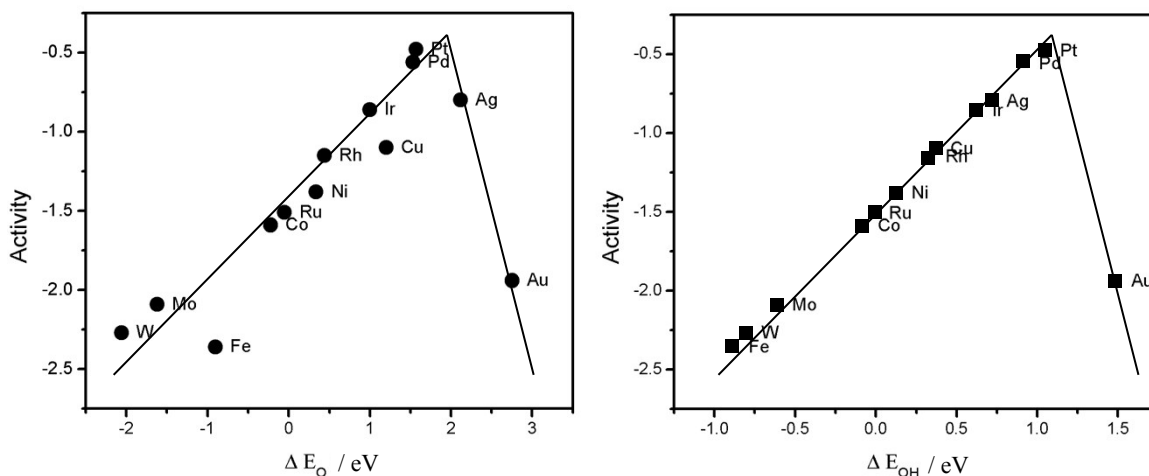


Figure S1 - Trends in oxygen reduction activity plotted as a function of the oxygen binding energy and OH binding energy, Copyright 2004 American Chemical Society [J. K. Nørskov *et al J. Phys. Chem.*, **2004**, 108, 17886-17892.]

Ever since the first fuel cell introduced in 1842, in all fuel cell systems the most common catalytic material is platinum for both cathode and anode due to its marvelous performance in the adsorption and dissociation of gasses. Also, it is inert to most of chemicals. The above studies prove platinum to be the best catalyst for ORR among all other metals. However, it does not mean that platinum has the optimal catalytic material for ORR. It has some limitations for the applications due to its expensiveness and rareness, low methanol-tolerance, and carbon monoxide poisoning, *etc.* Most researchers are trying to go for alternative materials. Although, there are successful alternatives for anodes that have been developed and commercialized the commercially cheap cathode is still a conception. It should have a large improvement and the aim is to reduce the Pt loading or substitution of alternatives Pt free materials for Pt. In recent years, considerable improvements have been achieved and nowadays platinum loadings of as low as 0.1 mg cm⁻² has the same performance to pure Pt [Acres, G.J.K. *Electrocatalysts for fuel cells, Catalysis Today*, **1997**, 393-399].

Table S1 - Characteristics of different fuel cell systems

Fuel cell	Fuel	Electrolyte	Mobile ion	Working Temperature / °C	Mean Efficiency %
Alkaline fuel cell (AFC)	H ₂	Aqueous alkaline solutions KOH(aq)	OH ⁻	20-100	65
Phosphoric acid fuel cell (PAFC)	H ₂	Phosphoric acid	H ⁺	190-210	55
Proton Exchange Membrane (PEMFC)	H ₂	Proton conducting Polymer membrane	H ⁺	50-125	60
Direct Methanol /ethanol Fuel Cell (DMFC/DEFC)	CH ₃ OH, C ₂ H ₅ OH	Acids or solid polymer	H ⁺	50-120	30
Molten Carbonate Fuel Cell (MCFC)	H ₂ , CH ₄	Molten alkaline carbonates, K ₂ CO ₃ (l)	CO ₃ ²⁻	600	55
Solid Oxide Fuel Cell (SOFC)	H ₂ , CH ₄	O ²⁻ conducting ceramic oxides , ZrO ₂	O ²⁻	500–1100	60