

# **Development of Aluminum Air Batteries (*alkaline*) :**

***The challenges***

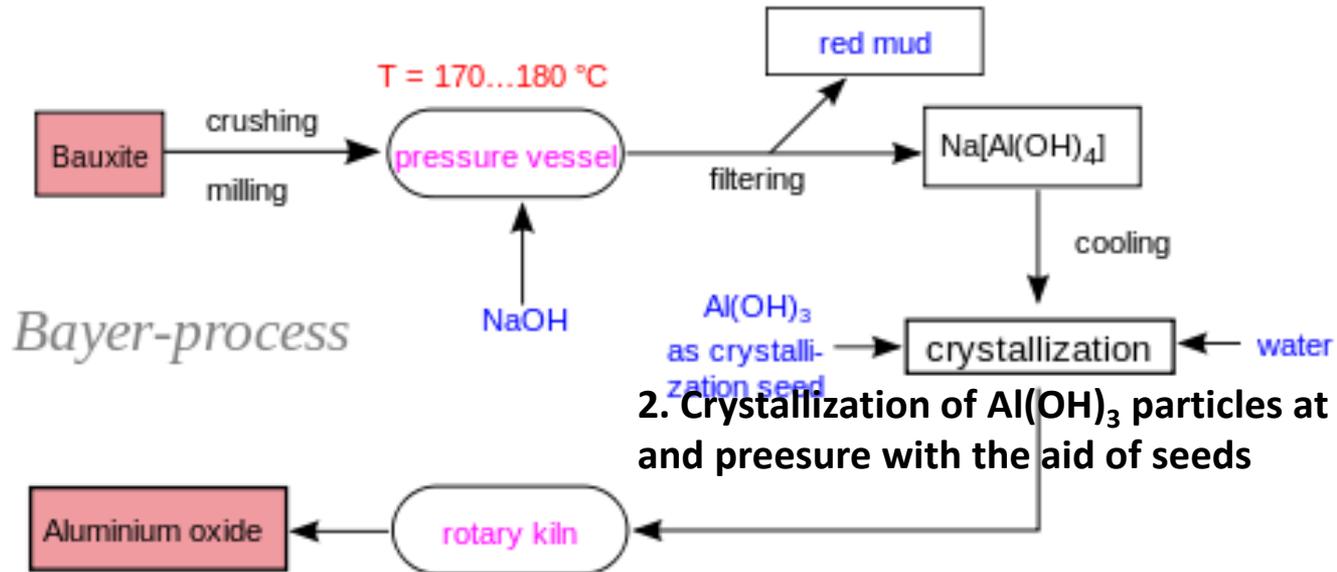
*We are going to review:*

- **Aluminum production – The Bayer Process**
- **The attractiveness of aluminum as an anode**
- **Aluminum Air Battery – the general system**
- **Aluminum Air Battery**
- **The Aluminum Anode**
- **The Air cathode**
- **The electrolyte**
- **Battery management**

# Aluminum production – The Bayer Process

- Aluminum is the most abundant metal in the Earth's crust . Still, its price is , relatively, not so cheap. Why?
- The main source for aluminum is “Bauxite”
- Bauxite is an aluminum ore that consists primarily of aluminum oxide and aluminum hydroxide minerals, mixed with two iron oxides, the clay mineral kaolinite and small amounts of anatase
- Aluminum is produced via Bayer process: Digestion , Crystallization, Calcination

## 1. Digestion in NaOH at elevated temperature and pressure

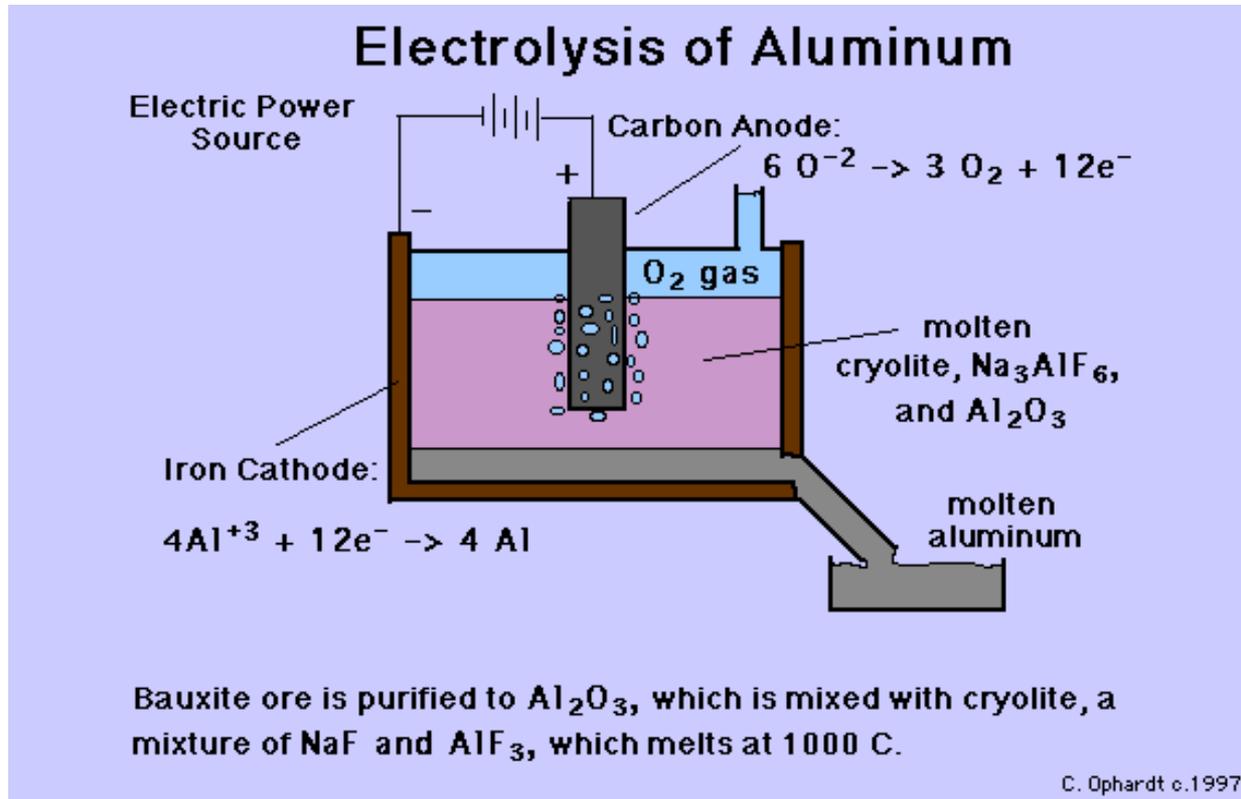


2. Crystallization of Al(OH)<sub>3</sub> particles at lower temperature and pressure with the aid of seeds

## 3. Calcination (>400°C) to obtain Al<sub>2</sub>O<sub>3</sub>

# Aluminum production – The Bayer Process

- The alumina particles are dissolved in a molten salt- cryolite at 1000°C.
- The Aluminum is then electrochemically reduced over an iron electrode.



- The price for 1Kg pure Aluminum is in the range of 2\$

# Why Aluminum is attractive as an anode material?

Aluminum possesses an impressive specific gravimetric capacity and more impressive volumetric capacity



Element	Capacity (Ah/g)
Lithium	3.86
Aluminum	2.98
Magnesium	2.20
Zinc	0.82

Specific gravimetric capacity

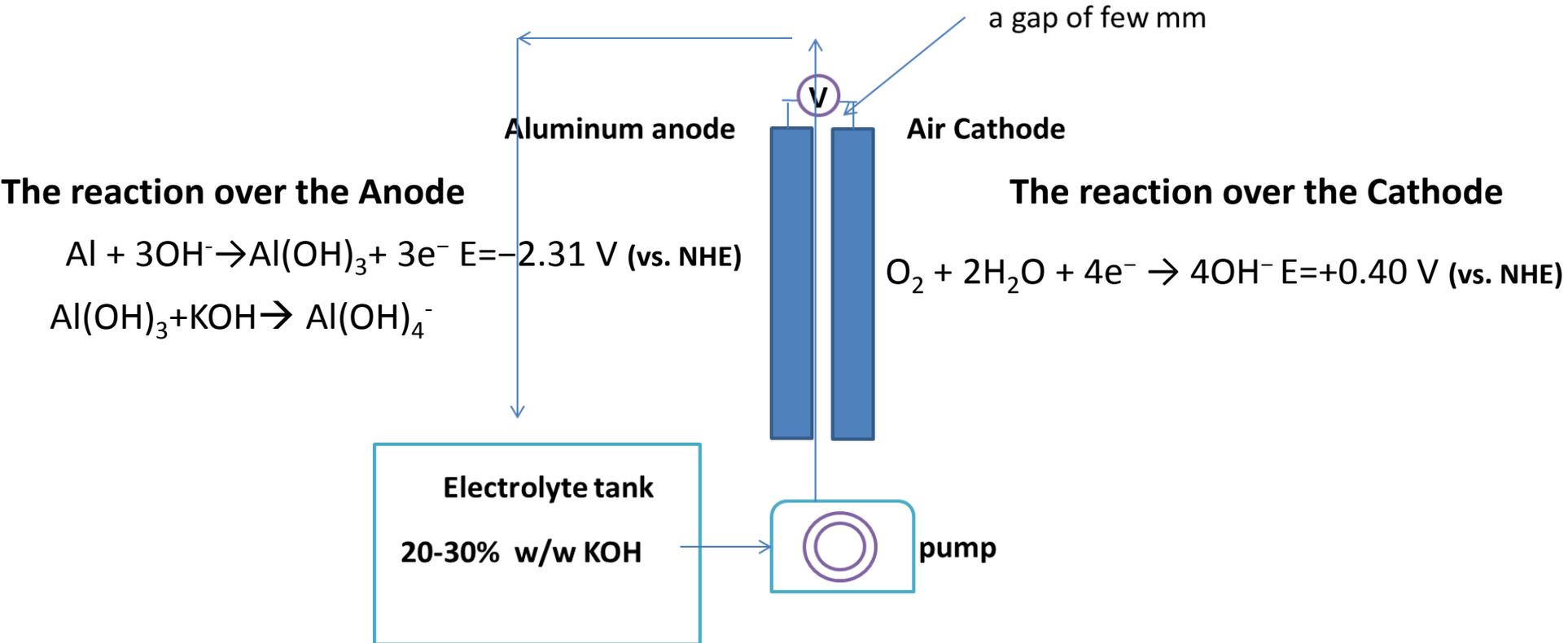


Element	Capacity (Ah/ml)
Aluminum	8.04
Zinc	5.85
Magnesium	3.83
Lithium	2.06

Specific volumetric capacity

# Aluminum Air Battery – the general system

## The battery components / structure



Overall reaction -  $4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al}(\text{OH})_3 \quad E = 2.71 \text{ V}$

- The practical potential obtained for a cell is around 1.2V
- Aluminum Air battery is a primary battery, where the anode is mechanically recharged (via Bayer process)

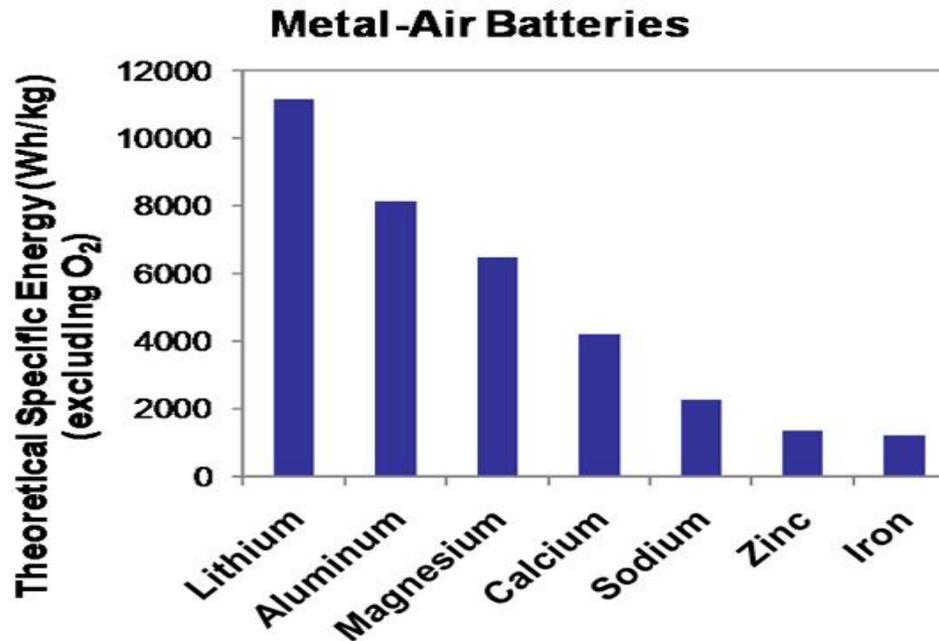
# The potential performance of Aluminum Air Battery

## Aluminum Air battery vs. metal air batteries– theoretical performance

- In theory Aluminum posses energy density as high as  $\sim 8\text{kWh/Kg}$  (!)
- 
- In practice, Aluminum prides  $\sim 1.3\text{ kWh/Kg}$

### Al in electric vehicle?

- In a **rough estimation** of  $10\text{kWh}/100\text{km}$ ,  $10\text{Kg}$  of aluminum may be equivalent to  $\sim 130\text{km}$  when considering aluminum as a fuel.



Theoretical specific energy for Metal Air batteries (normalized to the metal weight)

## **Aluminum Air Battery – The Aluminum Anode**

We will focus on the most two challenging issues regarding the aluminum anode:

1. Over - potentials.
2. Minimum self discharge ( or corrosion) – high columbic efficiency

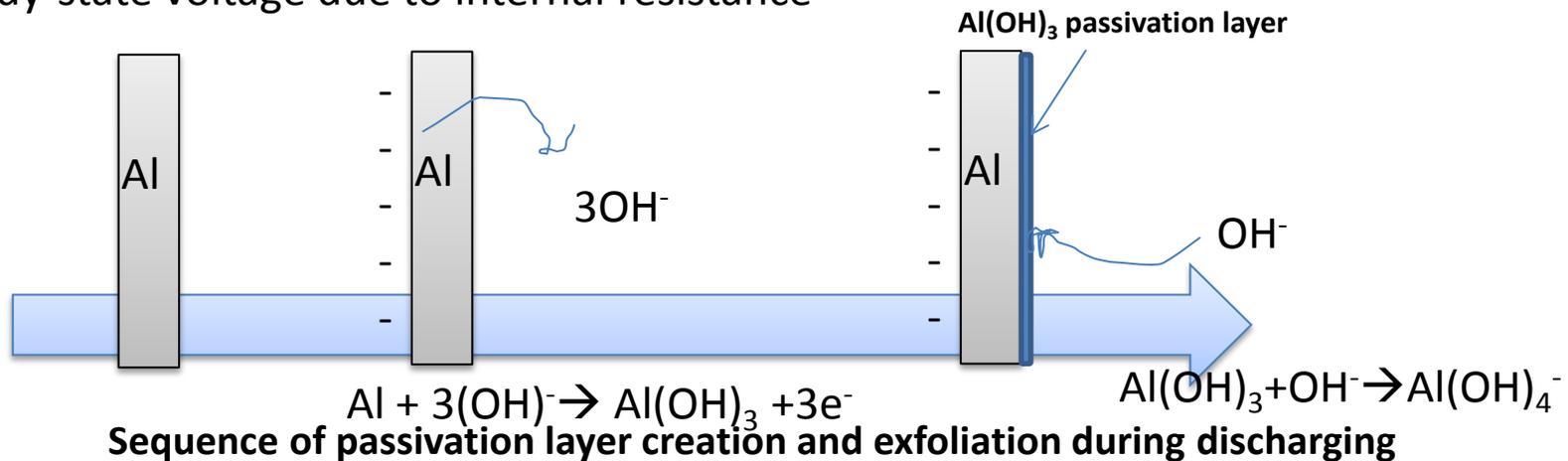
## Aluminum Air Battery – The Aluminum Anode

### Aluminum Anode potential in alkaline solution

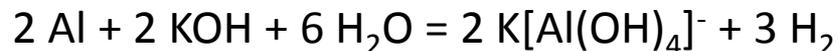
Thermodynamically, aluminum should exhibit a potential of  $\sim -2.35$  V (vs. NHE electrode) .

Practically aluminum anode operates at much lower potential because:

1. Aluminum is normally covered by an oxide film which causes a delay in reaching a steady-state voltage due to internal resistance



2. Aluminum undergoes a parasitic corrosion reaction, resulting in less than 100% utilization of the metal and the evolution of hydrogen.

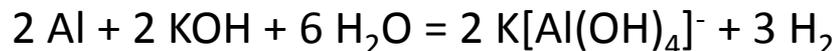


**Hydrogen evolution reaction by Al in KOH electrolyte**

# Aluminum Air Battery – The Aluminum Anode

## Anode corrosion

- Aluminum is thermodynamically unstable in an alkaline electrolyte and reacts with the electrolyte to generate hydrogen



**Hydrogen evolution reaction by Al in KOH electrolyte**

This parasitic corrosion reaction, or self-discharge, degrades the Coulombic efficiency of the anode and must be suppressed in order to minimize the capacity loss.

- Operating the battery at high currents (>100mA) results with higher coulombic efficiencies (

Table 3

Corrosion current of the ALCAN, 5N and 3N5 aluminum alloys in 4 M NaOH containing 0.05 M Na<sub>2</sub>SnO<sub>3</sub> and 20 g/l Al(OH)<sub>4</sub><sup>-</sup> at 60 °C

	ALCAN	5N	3N5
Open circuit potential			
$E_a$ (V vs. Hg/HgO) at $I = 0$	-1.87	-1.79	-1.78
$I_{\text{corrosion}}$ (mA/cm <sup>2</sup> )	12.1	13.5	15
$E_a = -1.65$ V vs. Hg/HgO			
$I_{\text{total}}$ (mA/cm <sup>2</sup> )	75	65	55
$I_{\text{corrosion}}$ (mA/cm <sup>2</sup> )	2.4	3	5.3

The difference at corrosion rate as a function of current densities for typical aluminum anode

# Aluminum Air Battery – The Aluminum Anode

## Anode corrosion

There are two ways to improve the anode behavior:

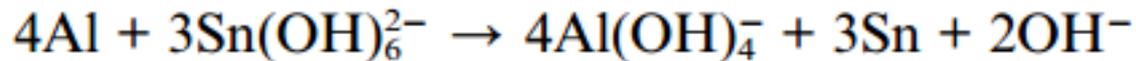
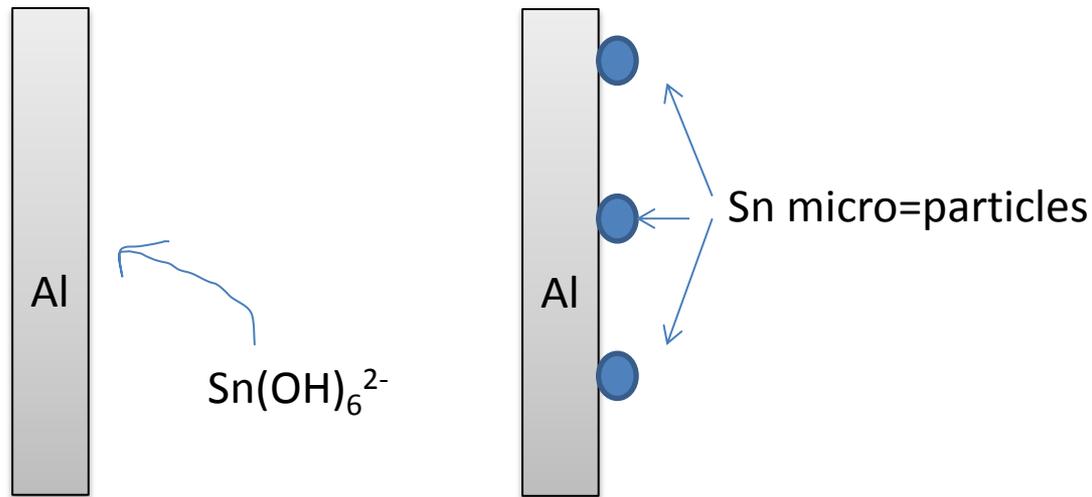
- One is doping the aluminum with other elements in order to render it less corrodible in the electrolyte- Elements which posses high overvoltage for hydrogen evolution are Ga, In, Sn, Zn, Mg, Ca, Pb, Hg, Mn
- The second and the cheaper one is to modify the electrolyte by adding inhibitors, additive agents or complexing agents in order to make the electrolyte less corrosive, as we will see on the next slide.

# Aluminum Air Battery – The Aluminum Anode

## Anode corrosion

For example – Stannate ( $\text{Sn}(\text{OH})_6^{2-}$ )

Additives which can be reduced and deposited by the aluminum anode (such as  $\text{Sn}(\text{OH})_6^{2-}$ ) are introduced to the electrolyte

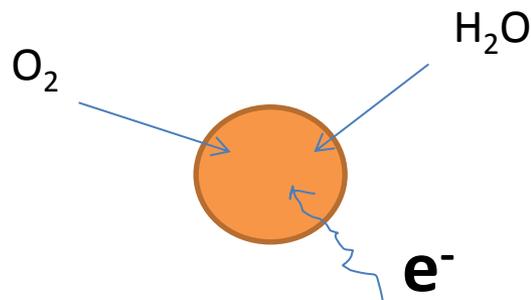


**Illustration of reduction of tin ions over the aluminum which results with microparticles deposition of tin over the anode**

## The Air cathode

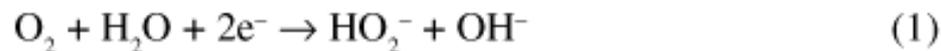
### (ORR reaction)

- Gas diffusion electrodes (GDE) are electrodes with a conjunction of a solid, liquid and gaseous interface, and an electrical conducting catalyst supporting.



***The triple point***

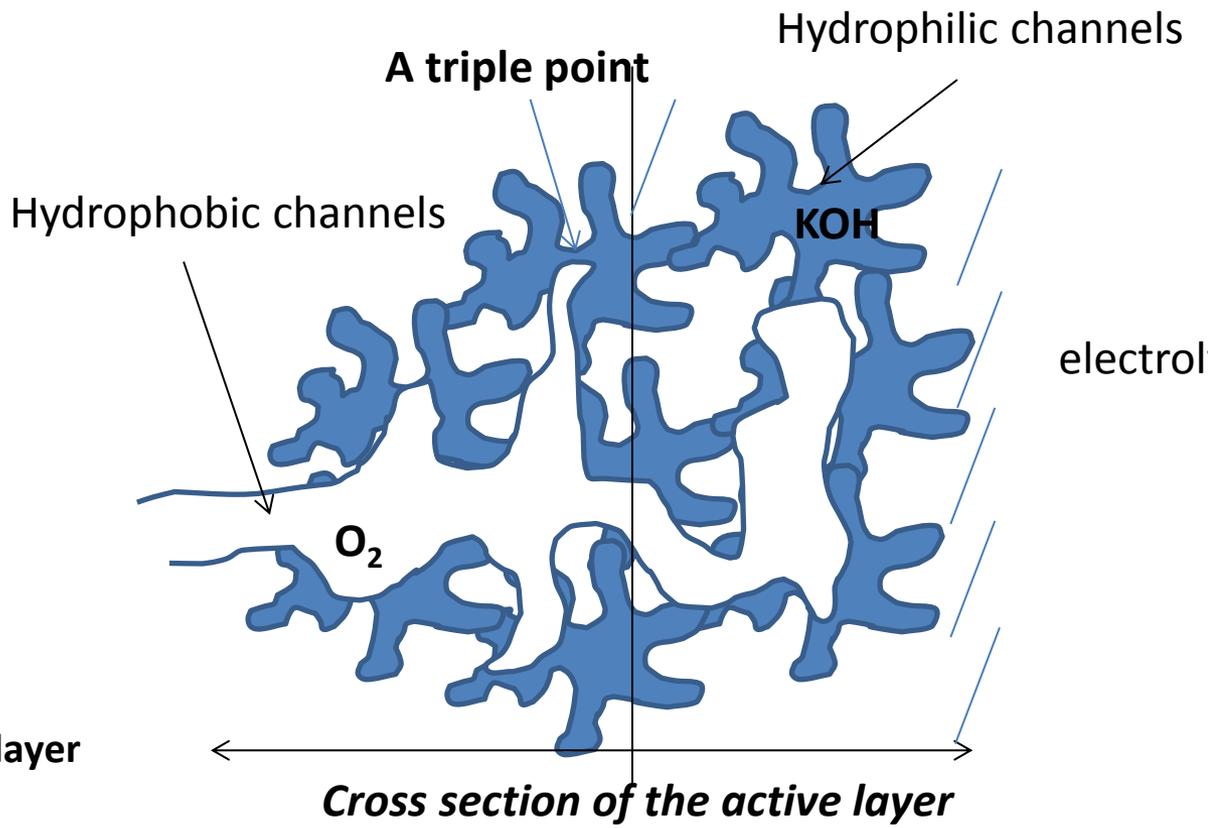
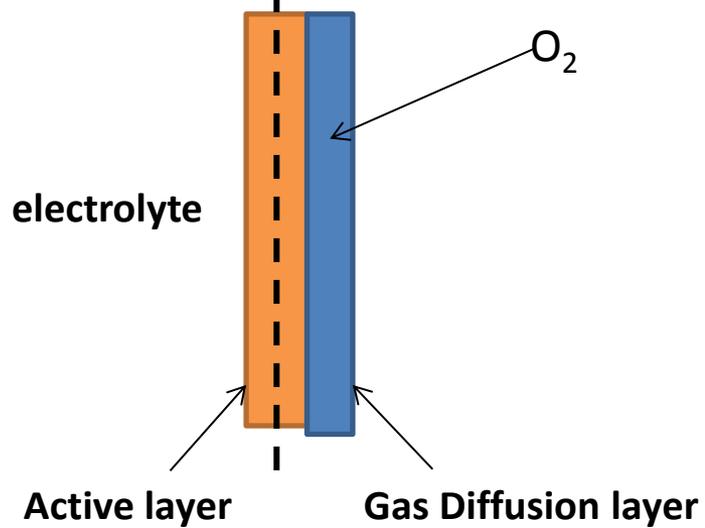
- For most of the catalyst in alkaline media, the ORR is a complex process involving four coupled proton and electron transfer steps



# The Air cathode

## Typical structure

Nickel mesh current collector



- The GDL supplies the reactant gas to the AL and prevents the liquid electrolyte from passing through the electrode. The GDL is usually made of porous PTFE.
- The active layer (AL) contains the catalyst which is usually supported on carbon black and bonded together with PTFE.
- Typically the AL will contain between 2 and 25% PTFE
- The AL enables multiple three-phase contact points

# The Air cathode

## Typical ORR catalyst in alkaline environment

**Table 2**  
Cathode performance using different catalysts with air.

Catalyst	KOH Temperature (°C)	KOH Concentration (M)	Potential vs. Hg/HgO (V)	Current density (mA cm <sup>-2</sup> )	Source
Pt/CNT/C 100 μg cm <sup>-2</sup>	25	6	-0.2	125	[48]
			-0.5	520	
Pr <sub>0.8</sub> Ca <sub>0.2</sub> MnO <sub>3</sub> /C 50 wt.%	60	8	-0.1	115	[144]
			-0.15	260	
CoTMPP/C Not known	25	5	-0.1	140	[71]
			-0.2	350	
			-0.25	500	
MnO <sub>2</sub> /C 3.63 mg cm <sup>-2</sup>	25	8	-0.2	91	[154]
			-0.5	440	
LaMnO <sub>3</sub> /C 6.9 mg cm <sup>-2</sup>	60	8	-0.08	300	[155]
			-0.1	400	
MnCo <sub>2</sub> O <sub>4</sub> /C 14 mg cm <sup>-2</sup>	60	6	-0.1	150	[152]
			-0.2	300	
Ag/C 47 mg cm <sup>-2</sup>	70	7	-0.1	250	[118]
			-0.2	540	

- The common catalysts for ORR in alkaline media are **platinum, silver, manganese oxide, manganese cobalt oxide** Recently, perovskite and spinel structures are considered.

## The Air cathode

2 Major issues concerning the air cathode in aluminum air battery

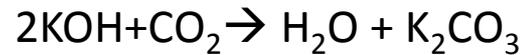
1. CO<sub>2</sub> effect

2. Weeping and flooding effect

## The Air cathode

### CO<sub>2</sub> effect

- Among time, the alkaline electrolyte exposed to the ambient, may react with CO<sub>2</sub> from the air to form potassium carbonate



- The formation of potassium carbonate is much more severe when tends to occur within the air cathodes channels.
- When the carbonate concentration reaches certain level it may precipitate within the hydrophilic channels and block the access for oxygen
- Scrubbers for CO<sub>2</sub> capture mounted on metal batteries were suggested but the significant increase at the weight and volume should be considered.

## The Air cathode

### **Weeping / Flooding**

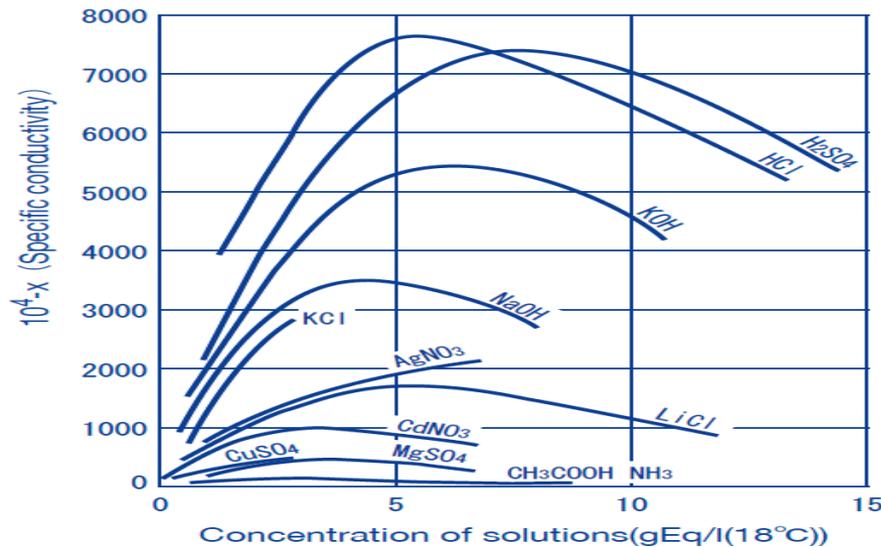
- As a consequence of a difference at a physical characteristic between the electrolyte within the air cathode channels and the electrolyte in the bulk (concentration difference), high pressure in the channels could be developed as a drag of water
- This may result with the so called “weeping” or “flooding” where electrolyte penetrates to the “hydrophobic zone”.
- Electrolyte in the hydrophobic zone impede oxygen accessibility to the three phase point and cause to degradation in the battery performance.

## The Air cathode

## The electrolyte

Potassium hydroxide solution (KOH) is almost exclusively used as the electrolyte because:

1. it has a higher ionic conductivity than sodium hydroxide solution.
2. potassium carbonate has a higher solubility product than sodium hydroxide, which renders the former less likely to precipitate



N.Kameyama 「Denkikagaku no Riron Oyobi Ouyou Part I」  
(Theory and Applications of Electrochemistry Part I), P31.1963. (Maruzen Pub.)

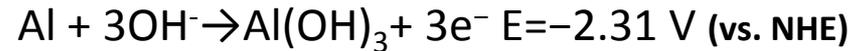
**Specific conductivity vs. concentration of several electrolytes**

## The Air cathode

## The electrolyte

### Electrolyte degradation

- The anode product, i.e.  $\text{Al(OH)}_3$  proceed to react with the electrolyte to form aluminate ion- ( $\text{Al(OH)}_4^-$ )



- This causes to a decrease at the  $[\text{OH}]^-$  at the expense of  $\text{Al(OH)}_4^-$ .
- The decrease at the  $[\text{OH}]^-$  concentration and electrolyte conductivity lead to battery failure.
- The electrolyte can “absorb” between 300-400 Ah/l till it should be replaced, way far before the aluminum anode should be replaced.

## The Air cathode

## The electrolyte

### Electrolyte degradation

### Electrolyte regeneration

- In fact , the reaction  $\text{Al(OH)}_4^- \rightarrow \text{Al(OH)}_3 + \text{OH}^-$  should occur spontaneously when the aluminate concentration reaches a certain level
- This reaction is *very slow* and cannot compete with the rate of which the aluminum “produces” aluminate
- 
- This reaction can be hasten by using  $\text{Al(OH)}_3$  seeds.
- The seeds should facilitate the nucleation process and hence, regenerate the electrolyte either in the battery or outside the battery (like in the Bayer process).

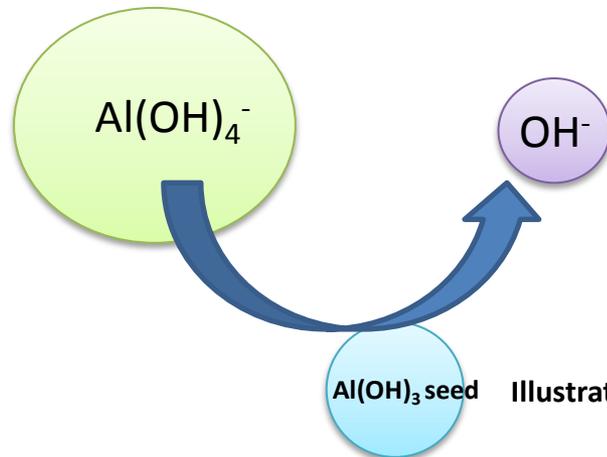
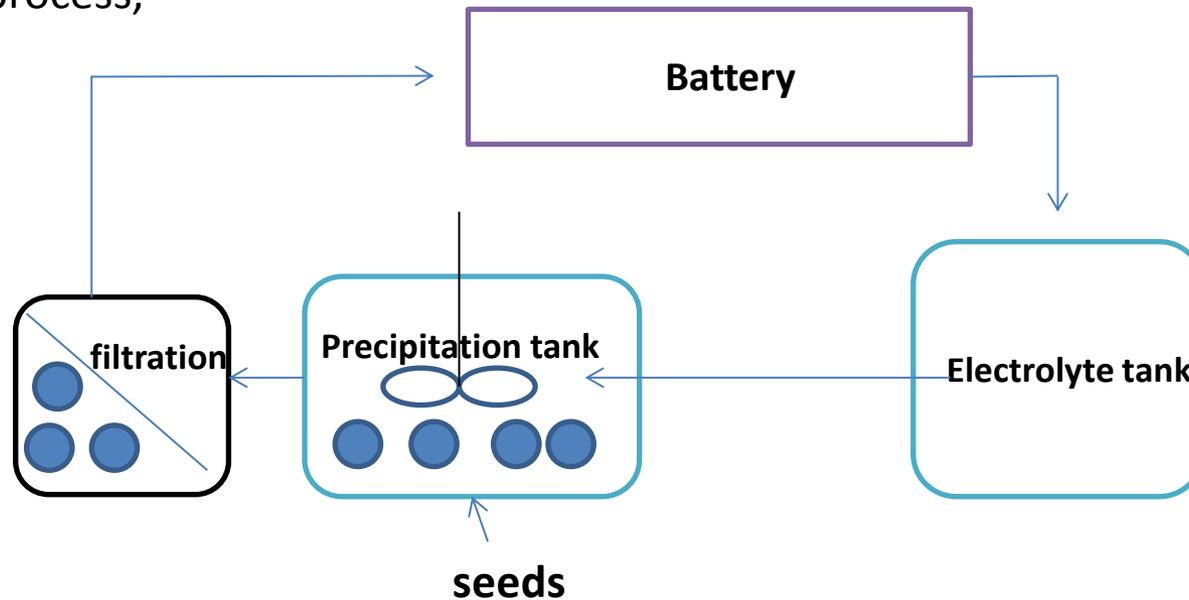


Illustration of precipitation of aluminate with the aid of  $\text{Al(OH)}_3$  seeds

# The electrolyte

## Electrolyte degradation

- Introduction of seeds increases the weight and volume of the system.
- The precipitants are in the form of a paste and not easy to be filtered out
- Special micro-filtration apparatus should be assembled, else the precipitants will adhere to the battery components.
- However, the product,  $\text{Al}(\text{OH})_3$  can proceed to aluminum production in the Bayer process,



Schematic illustration of electrolyte regeneration with seeds

## Battery management

### The benefit of electrolyte circulation

- circulation of the electrolyte enables the  $\text{CO}_2$  removal.
- The anode reaction is exothermic. Heat management is mandatory and it could be achieved by electrolyte circulation.
- The circulation of electrolyte prevents the build up of  $\text{H}_2$  bubbles adjacent the anode.

# Battery management

## “Start-Stop”

- Start – Stop of the battery is still one of its challenge as far as we are aim for electric vehicle..
- At zero current the corrosion is maximal and very dangerous.
- Evacuating all the electrolyte from the battery during stopping is unacceptable, since entrapped droplets of KOH continue to react with aluminum anode leaving beyond “ugly” pits.

Questions?