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Practical Challenges Associated with Catalyst Development for the Commercialization of Li-air Batteries

Myounggu Park[1,*], Ka Young Kim[2], Hyeryun Seo[2], Young Eun Cheon[2], Jae Hyun Koh[2], Heeyoung Sun[1], and Tae Jin Kim[2]

[1] *Advanced Battery Team, Battery R&D Center, SK innovation 325 Exporo, Wonchon-dong, Daejeon 305-712, South-Korea*
[2] *Catalyst Laboratory, Catalyst & Process R&D Center, SK innovation 325 Exporo, Wonchon-dong, Daejeon 305-712, South-Korea*

ABSTRACT:

Li-air cell is an exotic type of energy storage and conversion device considered to be half battery and half fuel cell. Its successful commercialization highly depends on the timely development of key components. Among these key components, the catalyst (i.e., the core portion of the air electrode) is of critical importance and of the upmost priority. Indeed, it is expected that these catalysts will have a direct and dramatic impact on the Li-air cell's performance by reducing overpotentials, as well as by enhancing the overall capacity and cycle life of Li-air cells. Unfortunately, the technological advancement related to catalysts is sluggish at present. Based on the insights gained from this review, this sluggishness is due to challenges in both the commercialization of the catalyst, and the fundamental studies pertaining to its development. Challenges in the commercialization of the catalyst can be summarized as 1) the identification of superior materials for Li-air cell catalysts, 2) the development of fundamental, material-based assessments for potential catalyst materials, 3) the achievement of a reduction in both cost and time concerning the design of the Li-air cell catalysts. As for the challenges concerning the fundamental studies of Li-air cell catalysts, they are 1) the development of experimental techniques for determining both the nano and micro structure of catalysts, 2) the attainment of both repeatable and verifiable experimental characteristics of catalyst degradation, 3) the development of the predictive capability pertaining to the performance of the catalyst using fundamental material properties. Therefore, under the current circumstances, it is going to be an extremely daunting task to develop appropriate catalysts for the commercialization of Li-air batteries; at least within the foreseeable future. Regardless, nano materials are expected to play a crucial role in this field.

Keywords: Catalyst, Li-air cells, Commercialization

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1. INTRODUCTION

In Fig. 1[1-9] a series of remarkable events pertaining to battery inventions (including fuel cells) is depicted in a chronological manner. The Li-air battery was first invented in 1996, utilizing polymer electrolyte (the non-aqueous Li-air cell), although the concept itself was formulated in 1976. However, until today this technology has not been commercialized due to the insurmountable barriers stemming from the lack of appropriate materials used in key components. As of today, Li-ion batteries have become an icon in the field of mainstream batteries. Ever since 1991, their prosperity has been the result of rigorous applications, ranging from electronic devices to electric cars (EVs).

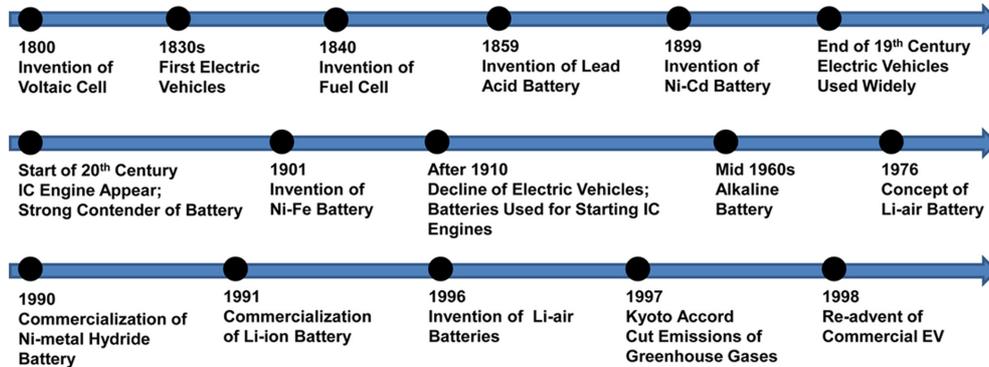*Corresponding author. Tel.: +82-42-609-8756
E-mail address: myoungupark@sk.com

Fig. 1. Brief History of the Invention of Batteries and Fuel Cells.[1-9]

The technologies related to Li-ion batteries, such as the synthesis and manufacturing of active materials, separators, electrolytes, and cell assembly, have been rapidly developed over the years. However, focus on the Li-air battery and its recent revival should be noted.[10-12] Of course, there could be many reasons for this resurgence, but a rudimentary explanation can be found in the Ragonne plot (not shown here). The Ragonne Plot indicates the specific energy and power performance of a battery system. Specific energy density directly relates to how far an EV can travel. On the other hand, specific power density pertains to how much acceleration an EV can achieve. Currently, these two important performance descriptors demonstrate that the upper limits are going to be reached in the near future (around 2020) where Li-ion batteries are concerned. That is, a specific energy density of 250 Wh/kg. Furthermore, it should be noted that the anticipated maximum performance of the advanced Li-ion battery still cannot meet the requirements of pure electric vehicles. Therefore, it is reasonable to conclude that the need for the next generation batteries is imminent and indispensible. Thus, it is not all that surprising to see so many researchers and scientists within the battery community paying close attention to Li-air batteries due to high theoretical energy density (gasoline:12,200 Wh/kg while Li-air batteries provide 13,000 Wh/kg, based on the weight of Li metal only, and 5,200 Wh/kg based on the weight of Li metal and oxygen).[13] In addition to this, there is a high safety factor to consider, i.e., only one part of the active material is contained in the battery system. Thus, thermal runaway (or short circuit) is unlikely[13] in spite of the conceivable shortcomings of the Li-air battery system due to its dependency on oxygen in order to func-

tion. Note that this battery system cannot be used in oxygen-free environments such as outer space, implanted heart pacemakers, and underwater conditions.[14]

Previously, in an effort to better understand the overall status of Li-air battery research, the authors published a review article covering a rather broad scope of topics.[10] As a continuation of this effort, the authors undertook another round of review focusing on the catalysts and it is reported here. In this article, we mainly address the significance of catalysts (i.e., air cathodes), which is unfamiliar to the conventional battery developer. The authors established the following three goals:

1. Understanding catalysts (fundamental concepts and synthesis methods)
2. Understanding the role of catalysts in Li-air batteries
3. Obtaining perspectives for the commercialization of Li-air batteries

The methodologies utilized to fulfill the above goals are described in the next section, followed by the results. The perspectives gleaned by the authors are from a battery industry viewpoint, and thus may differ from perspectives held by other researchers facing different circumstances.

2. METHODS

Peer-reviewed journal articles are invaluable sources of information. Book chapters have also been consulted. The authors appreciate all of the pioneering research efforts exerted by both previous and contem-

porary researchers. A web-based search engine has been mainly utilized.[15]

3. RESULTS

3.1. Key Concepts Related to Catalysts

It has been shown that the catalyst in an air electrode is a crucially important component, as it can dictate the power and energy density, energy efficiency and cycle life of Li-air batteries.[128] In this section fundamental concepts related to catalysts are addressed in a succinct manner.

General concept. A catalyst is normally defined as a material that can change the kinetic rate of a chemical reaction while the catalyst itself doesn't change.[16] Changing the kinetic rate indicates the acceleration or deceleration of the rate induced by the function of a catalyst. For most cases, however, the catalysts are used to accelerate the reaction rates. The catalyst plays the role of reducing the activation energy of a specific reaction and enhancing the reaction rate. For non-catalytic reactions, products are made by the collisions between reactive molecules. On the other hand, catalytic reactions occur through the adsorption of reactant molecules and desorption of product molecules.

Constituents of catalyst system. A catalyst is normally comprised of an active material and a supporting material. The active material is deposited on, or chemically bounded with, a porous support that has a large surface area. An active material is directly related to a chemical reaction rate, and various materials are used such as metals, metal oxides, and metal sulfides. Sometimes "Promoters" (or additives) are added into a catalyst system. The promoters have no catalytic activity, but they can affect the activity of a catalyst, either chemically or electronically.

Major properties of catalysts. The important properties of a catalyst are: activity, selectivity, and lifetime.[17-19] The activity refers to the ability of a catalyst to convert reactant molecules at a single active site. Selectivity is the fraction of a desired product among all the products. Selectivity is concerned when a reactant can be converted to several products, or when a desired product is in an intermediate stage and then might be converted into other materials. Lifetime is of great interest, especially from a cost reduction point of

view. Catalysts lose their initial activity due to various reasons including coking, poisoning and sintering.

Types of catalyst reactions. Generally, there are two types of catalytic reactions: oxidation-reduction reactions (electronic) and acid-base reactions (ionic).[20] Oxidation-reduction type reactions include oxidation, reduction, hydrogenation, dehydrogenation and hydrogenolysis (catalyzed by solids possessing free or easily excited electrons, i.e., metals), while acid-base type reactions include polymerization, isomerization, cracking, dehydration, alkylation, halogenations and dehalogenation (catalyzed by acidic or basic properties).

Surface reactions on catalysts. For heterogeneous catalysts, the surface reaction proceeds through: (1) diffusion of reactant molecules into the catalyst, (2) adsorption of the diffused reactants on the catalyst surface, (3) reaction between adsorbed molecules, (4) desorption of the product molecules from the catalyst surface, and (5) diffusion of the products into the bulk stream. Diffusion can be divided into "external diffusion" and "internal diffusion". Adsorption, desorption, and reaction are affected by chemical properties, whereas diffusion is affected by physical properties, such as fluid velocity and pore structure (Fig. 2). Therefore, it is of great importance to understand the reactions at the internal and external surface of catalysts, along with the effects of pore structure, for the further development of Li-air cathode catalysts.

Surface area of catalysts. The total surface area of a catalyst is the sum of all the surface areas of pores with various sizes. For a given mass, the surface area of a catalyst is inversely related to the size of the
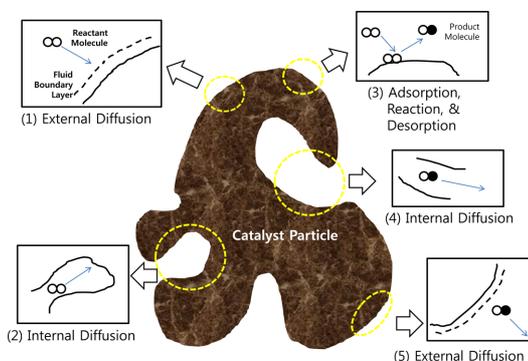

Fig. 2. Surface Reaction on Heterogeneous Catalysts.

pores. Thus, the surface area of a catalyst having a high percentage of small pores is larger than that of a catalyst having a high percentage of large pores. Also there are two kinds of pores depending on the formation process i.e., interstitial and internal pores. The interstitial pores are formed between the primary particles within the aggregated particles, and the internal pores are formed inside the primary particles. Therefore, external surfaces include all the outer surfaces of catalysts and aggregated catalysts, while the internal surface is composed of all the surfaces of the internal pores.[21]

3.2. Synthesis Methods of Catalysts

External and internal morphologies of catalysts synthesized by various methods play a crucial role in the catalytic activities. When it comes to catalyst synthesis it can be broadly classified into two main methods–impregnation and colloidal, both of which are well

Table 1. Features of the Impregnation Method[29-34]

Item	Description	Note
Advantages	• High surface area • Simplicity	
Disadvantages	• Low activity • Difficult dispersion control • Broad particle size distribution • High aggregation	• High metal loading • Lower activity
Precursors	• H_2PtCl_6, $RuCl_3$	• Chloride Poisoning • Reduction of Dispersion, Catalytic Activity, Stability
	• $Na_6Pt(SO_3)_4$, $Na_6Ru(SO_3)_4$ • $Pt(NH_3)_2(NO_2)_2$, $RuNO(NO_3)_x$ • $Pt(NH_3)_4(OH)_2$, $Pt(C_8H_{12})(CH_3)_2$ $Ru_3(CO)_{12}$	• Increase of Dispersion • Catalytic Activity
Metal contents	• Pt 10-60 % • Pt 40 %, Ru 20 %	
Reducing agents	• Liquid • Gas	• $Na_xS_2O_3$, $NaBH_4$, $Na_4S_2O_5$, N_2H_4, CH_2O_2, H_2
Variations	• Precursor • Carbon • Temperature • Pt content	• Structural & Electrocatalytic Properties • Size distribution • Activity • Size

documented for noble metal based catalysts (e.g., Pt, Pd, Ru). Meanwhile, sputtering and heat treatment methods[22-26] have been newly explored in transition metal based catalysts (e.g., Fe, Co, Mo) and metal-free carbon catalysts.[27,28] In this section two main synthesis methods are briefly summarized.

Impregnation method. Impregnation is the most widely utilized method, due to its simplicity, high dispersion on the support, and the easy scale-up for mass production. Features of impregnation method are summarized in Table 1.[29-34] This method is widely used for preparing ORR catalysts; e.g., the carbon supported Pt and Pd nanoparticles.[35,36] As for the general procedures, it is as follows: the calculated amount of active metal precursor (e.g., H_2PtC_{16} $_xH_2O$, RuC_{13}, $Na_6Pt(SO_3)_4$, and $Na_6Ru(SO_3)_4$) is dissolved in a medium, such as alcohol and/or water. For a better dispersion of the metal precursor, a citric acid can be added as a stabilizer.[37] The solution and carbon support are mixed with mild stirring. The carbon support loaded with the active metal precursor is then incubated in an oven at 100°C overnight, and then treated with various reducing agents. Depending on the phase of the reducing agent, there are various methods including the hydrogen gas reduction method[31,32] and the liquid reduction method.[29,35,38-41] Recently carbide based catalysts (e.g., Pt-W_2C/C, $Co_6Mo_6C_2$/C) prepared by combining the impregnation and microwave heating methods have been intensively studied.[41-44]

Colloidal method. The major disadvantages of the impregnation method are related to low activity, broad particle size distribution, and tendency to be easily aggregated. To overcome these drawbacks, the colloidal method has been developed, and is often used in the studies of Pt/C, Pd/C, and PtRu/C catalysts[45-47] (Fig. 3). A general description of the colloidal procedure[48-50] is as follows (Table 2[46,51,52]): 1) preparing a colloidal solution containing metal nanoparticles with stabilizers (e.g., tetraoctylammonium bromide (TOAB), Polyvinylpyrrolidone (PVP), and 1-propanol) and 2) depositing metal nanoparticles onto the surface of carbon supports.

3.3. Roles of Catalysts in Li-air Cells

Based on the nature of the electrolytes and its reaction products, Li-air cells can be classified broadly into two types;[53] i.e., non-aqueous and hybrid (also see Fig.
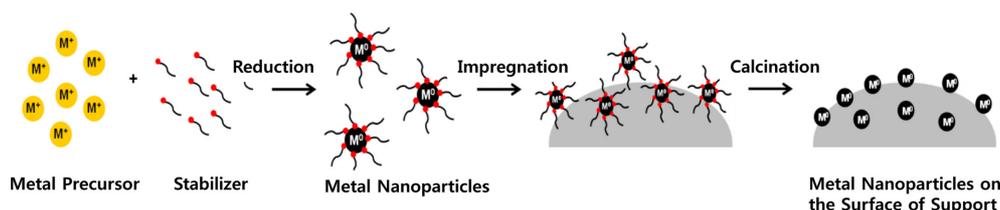
Fig. 3. General Process of the Impregnation Method.

Table 2. Features of the Colloidal Method[51,46,52]

Item	Description	Note
Advantages	• Smaller Particle Size • Narrow Size Distribution • Higher Degree of Crystallinity • Higher Dispersity • Low Aggregation	
Disadvantages	• High Cost	• Expensive Stabilizer • Extra Washing Step • Needed Easily Rinsed Surfactant
Metal Contents	• Pt:Ru = 1:1 or 1:3	
Stabilizers	• Polymer, Block copolymers, Solvents, Long-chain Alcohols, Surfactants, Organometallics	• Dodecyldimethyl(3-sulfo-propyl) ammonium hydroxide (SB12) • Polyvinylpyrro-lidone (PVP) • Tetraoctylammonium bromide (TOAB)
Colloidal Sources	• Metal Oxide • Organometallic	
Variations	• Rate of Nucleation (particle growth) • Reducing Atmosphere (N2 or Air)	• Colloid Size • Narrow Size Distribution • High Activity

Table 3. Comparison of Li-air Cells: Non-aqueous vs. Aqueous Electrolytes[54]

	Non-aqueous electrolyte	Aqueous electrolyte
Maximum Capacity	• Blocking of carbon pore due to precipitation of Li_2O/Li_2O_2	• LiOH is highly soluble • Amount of metallic Li use
Reaction Zone Models for ORR	• Two-phase reaction zone	• Three-phase reaction zone
Catalysts	• MnO_x, noble metal and their oxide • Combinations of MnO_2 and metals • Simple oxides of Fe, Co, Ni, Cu	• noble metal • bimetal of noble metal
Function of Catalyst System	• Alternation of morphology of Li-oxide precipitation	• Control of binding energy of metal-oxygen

1 and 2 in ref.[10]). The roles of catalysts are expected to differ for each type of Li-air cell (Table 3 [54]).

Roles of catalysts in non-aqueous Li-air cells. The reaction mechanisms at the interfaces between the air-cathode and the electrolyte are inevitably affected by Li_2O_2 formed inside the pores. Micro-pores and some of meso-pores are blocked by Li oxide during cycling and the surface area of those pores will not be accessed by either air or electrolyte, making them unavailable for the electrochemical reaction. Thus the manipulation of the carbon support's pore structure are observed to be more central issues[55-58] although active catalyst materials themselves are researched a lot. Thus the selection of appropriate support materials is quite

significant. To fulfill these unique requirements, carbon blacks (e.g., Acetylene Black, Vulcan XC-72, Ketjen Black) have been mainly adopted. The properties of a carbon support, such as the specific surface area, porosity, morphology, surface functional groups, electronic conductivity, and corrosion resistance, must be down-selected in order to make an appropriate catalyst system. Currently Vulcan XC-72 with a surface area of approximately 250 m^2g^{-1} has been widely utilized.[21,59] However, note that an accessible and sufficiently large surface area of carbon blacks for maximum catalyst dispersion has been argued to be a necessary, albeit insufficient condition, for obtaining optimized carbon supported catalysts.[60-67] Overall, a salient observation is that the main roles of catalysts seem to control the morphology and accommodate Li_2O_2.[68]

Roles of Catalysts in Hybrid Li-air cells. In hybrid Li-air cells, the role of catalysts can be clearly defined; it is to control the binding energy between oxygen species and metal surfaces. Because bound oxygen species are intermediates in the oxygen reduction reaction, the level of binding energy can have significant effects on catalytic activity.[69] For metal surfaces that bind oxygen too weakly, the rate is limited by either the dissociation of O_2 or the transfer of electrons to adsorbed O_2, i.e., possible rate-limiting step can be dictated by different oxygen reduction mechanisms. Also, if Pt binds oxygen too strongly the catalytic activity is negatively affected. Therefore, in order to achieve better electrocatalystic activity, optimal binding energy should be acquired for each particular catalyst system.[70] A major advantage of the binding energy approach (utilizing the characteristics of electronic structure; i.e., HOMO and LUMO), is to provide a way to predict the electrocatalytic activity of a metal surface.

3.4. Survey of Catalyst Research in Li-air Cells

Catalysts vs. overpotential. Overpotential (and capacity) values of non-aqueous and hybrid Li-air cells utilizing various catalysts are summarized in Table 4[13,71-91] and Table 5[53,92,133,154,164] respectively. Also refer to Fig. 4[130] for non-aqueous Li-air cells and Figs 5, 6, 7[93] for hybrid Li-air cells regarding discharge/charge plots and corresponding overpotentials. The results summarized in Table 4 imply that the dif-

Table 4. Catalysts Used for Non-aqueous Li-air Batteries[13,71-91]

Catalyst	Chemical Formula	Note[1), 3)]
Metal	• Pt	• Overvoltage (V): 0.45 (discharge) • Capacity (mAh/g): 470 (Pt)
	• Au/C[2)], Pt/C,	• Overvoltage (V): 0.6 (discharge), 0.8 ~ 1.2 (charge) • Capacity (mAh/g): 1250 (Au/C), 760 (Pt/C)
	• PtAu[7)]/C	• Overvoltage (V): 0.2 (discharge), 0.6 (charge) • Capacity (mAh/g): 1300
	• Pd/α-MnO₂[2)], Pd/β-MnO₂[2)]	• Overvoltage (V): 0.5 (discharge), 0.6 (charge) • Capacity (mAh/g): 257 ~ 550
	• Pt$_x$Co$_y$ (x:y = 4, 2, 1,0.5) alloy	• Overvoltage (V): 0.27 (discharge), 0.94 (charge) • Capacity (mAh/g): 2000 ~ 3000 depending on x and y
Carbon	• Carbon particle	• Overvoltage (V):0.3~ 0.4 (discharge), 1.0 ~ 1.2 (charge) • Capacity (mAh/g): 800 (vulcan), 1000 (super S carbon)
	• Nanotube	• Overvoltage (V): 0.6 (discharge), 1.3 (charge) • Capacity (mAh/g): 600
	• Nitrogen-doped Carbon	• Overvoltage (V): 0.2 (discharge), 0.6 (charge) • Capacity (mAh): 0.1
	• Graphene	• Overvoltage (V): 0.25 (discharge), 1.0 (charge) • Capacity (mAh): 2332
	• Nitrogen-doped CNTs	• Overvoltage (V): 0.5 (discharge), 1.2 (charge) • Capacity(mAh/g): 900
	• Diamond Like Carbon Thin film	• Overvoltage (V): 0.25 (discharge), 1.25 (charge) • Capacity (mAh): 2000

Table 4. Continued

Catalyst	Chemical Formula	Note[1]
Manganese Oxides	• α-MnO_2[5], β-MnO_2, γ-MnO_2, λ-MnO_2	• Overvoltage (V): 0.6 (discharge), 1.0 (charge) • Capacity(mAh/g): 1500 (α-MnO_2), 1000 (-MnO_2), 1875 (-MnO_2), 2375 (-MnO_2)
	• MnO_x/C	• Overvoltage (V): 0.5 (discharge), 1.0 ~ 1.2 (charge) • Capacity(mAh/g): 4400 (MnO_x/Norit), 3900 (MnO_x/Acetylene), 3400 (MnO_x/Super P)
	• $Na_{0.44}MnO_2$ Nanowire	• Overvoltage (V): 0.5 (discharge), 0.9 (charge) • Capacity(mAh/g): 12000
Li_2O Rich Phases	• Li_5FeO_4 ($5Li_2O\bullet Fe_2O_3$), $Li_2MnO_3\bullet LiFeO_2$ ($[Li_2O\bullet MnO_2]\bullet[Li_2O\bullet Fe_2O_3]$)	• Overvoltage (V): 0.5 (discharge), 1.2 (charge) • Capacity(mAh/g): 2680
Insertion materials	• MnO_2, V_2O_2, or CF_x and C Composite	• Overvoltage (V): 0.5 (discharge only), • Capacity(mAh/g): 900 (CF_x & C), 700 (V_2O_2 & C), 480 (MnO_2 & C)
Nano/nano[8), 9)]	• MnO_2/MWNT	• Overvoltage (V): 0.5 (discharge), 0.8 (charge) • Capacity(mAh/g): 1786
Perovskite	• $La_{0.8}Sr_{0.2}MnO_3$	• Overvoltage (V): 0.4 (discharge) • Capacity (mAh/g): 750
Metal Oxide	• Fe_2O_3, NiO, Fe_3O_4, Co_3O_4, CuO, $CoFe_2O_4$ • Mixture with S Carbon and Kynar	• Overvoltage (V): 0.4 (discharge), 0.9 ~ 1.3 (charge) • Capacity (mAh/g): 2700 (Fe_2O_3), 1600 (NiO), 1200 (Fe_3O_4), 900 (CuO), 1200($CoFe_2O_4$)
	• Co_3O_4/RGO[2]	• Overvoltage (V): 0.25 (discharge), 0.5 (charge) • Capacity (mAh/g): 15000
Pyrochlore Oxide	• RbRO, BiRO, Au/RbRO[2], RbRO/C • Chemical Formula: $(A_2B_2O_6O'_{1-\delta})$[4]	• Overvoltage (V): 0.3 (discharge), 1.2 (charge) • Capacity (mAh/g): 9900 ~ 8000 (RbRO, BiRO), 12000 (Au/RbRO), 10000 (RbRO/C)

1) Overvoltage and capacity values are based on the 1st discharge/charge cycle as reported in the literature
2) $'/C'$, $'/MnO_2'$, $'/RbRO'$ and $'/RGO'$ indicate that the support material are carbon, manganese oxide, lead ruthenium, and reduced graphene oxide respectively
3) Except otherwise explicitly described as 'bulk' materials in the report, we classify them as nano-sized materials
4) A = Pb or Bi, B = Ru or Ir
5) The prefixes, such as α-, β-, γ-, λ-, represent polymorphs of MnO_2
6) Except otherwise stated, all catalysts are monofunctional
7) PtAu is a bifunctional catalyst
8) Nano means nanostructured materials including nanoparticle, nanocrystals, nanowires, nanotubes, nanobelts and nanoflowers
9) $'Nano/nano'$ indicates that nano-size substrate materials are decorated with nano-size catalysts

ferent overpotential values on discharge/charge of non-aqueous Li-air cells may be related to the different orientations and morphologies of the oxide precipitates.[94-96)] Catalysts can affect the choice of the specific reaction path and thus affect the appearance and structure of the specific <oxygen|metal> intermediates.[97,98)] Among various catalyst systems for non-aqueous Li-air cells, PtAu (bifunctional catalyst) on carbon support and nitrogen-doped carbon are reported to have the best performance in terms of overpotential reduction.[99)] Also, various carbon materials are demonstrated as active catalysts;[12,85-88,100-102)] e.g., carbon nanotubes. Nonetheless, the consensus is that the effect of

various catalyst systems examined so far is obscure and there is no dominant one yet to be found. Controversy over the effects of catalysts can be partly ascribed to undetermined ORR and OER mechanisms.[103,128)] Most of all, the asymmetric discharge/charge curve (larger overpotential value for charge) is a distinctive feature indicating the significance and urgency of catalyst development for the charge process.

Different reaction paths of hybrid Li-air cells depending on catalyst materials and utilized electrolytes (alkaline or acidic) are summarized in Tables 6 and 7.[104,105)] Noble metals (especially Pt) have been proved to be the best so far for ORR.[106)] However, Pt

Table 5. Catalysts Used for Hybrid Li-air Batteries[53,92,133,154,164]

Catalyst	Chemical Formula	Note[1), 2)]
FePc[3)]	• FePc/GNS[4)]	• Overvoltage (V): 0.4 (discharge), 0.3 (charge) • Capacity(mAh/g): 632.4
	• FePc/CNT	• Overvoltage (V): 0.37 (discharge), 0.4 (charge) • Capacity(mAh/g): 865.6
	• FePc/AB[5)]	• Overvoltage (V): 0.5 (discharge), 0.6 (charge) • Capacity(mAh/g): 795.4
Pt	• Pt/CNT	• Overvoltage (V): 0.67 (discharge) • Capacity(mAh/g): 306
Pt	• Pt/C	• Overvoltage (V): 0.21 (discharge), 0.39 (charge) • Capacity(mAh/g): 2000
Spinel ($CoMn_2O_4$)	• $CoMn_2O_4$/C	• Voltage gap between discharge and charge (V): 0.8
Pt	• Pt Black	• Overvoltage[6)] (V): 0.3 (discharge), 0.2 (charge)

1) Overvoltage and capacity values are based on 1st discharge/charge cycle as reported in the literature
2) Generally, overvoltage and capacity are influenced by current density and catalyst loadings
3) FePc: Fe phthalocyanine
4) GNS: graphene nanosheet
5) AB: Acetylene Black
6) In this particular case, the hybrid Li-air cells were operating at 60°C

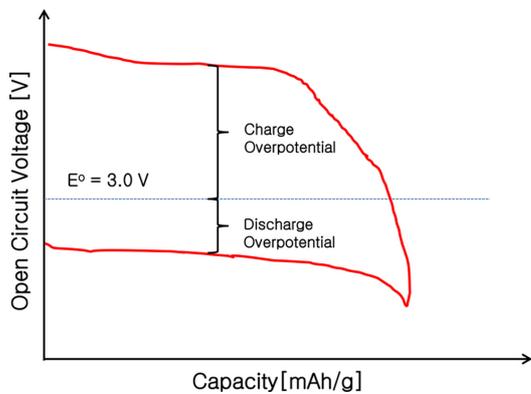**Fig. 4.** Cycling Performance of a non-aqueous Type Li-air Cell.[130]
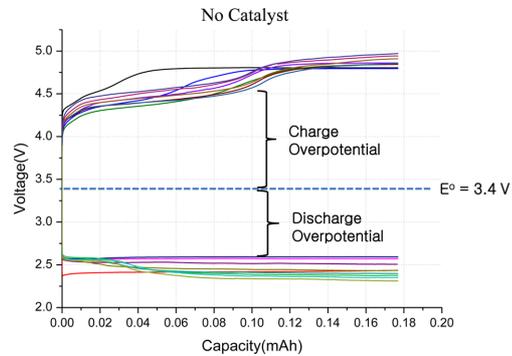

Fig. 5. Cycling Performance of a Hybrid Type Li-air Cell (Pt 0%).[93]
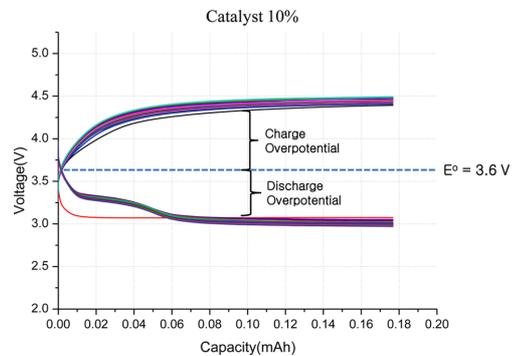
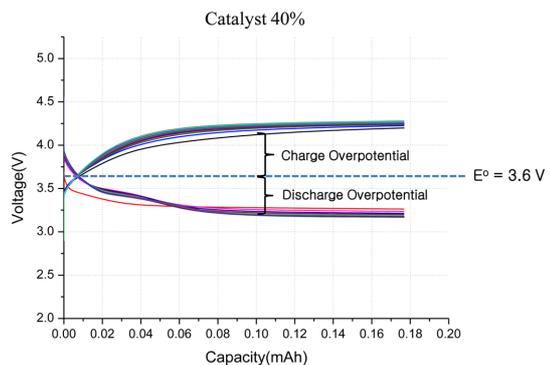**Fig. 6.** Cycling Performance of a Hybrid Type Li-air Cell (Pt 10%).[93]

Fig. 7. Cycling Performance of a Hybrid Type Li-air Cell (Pt 40%).[93]

catalyst has been found to be not effective for oxygen evolution reaction (OER) due to the formation of a stable oxide layer. In the case of Ru catalyst, it is better than Pt for oxygen evolution. However, Ru catalyst is still problematic due to corrosion limiting its lifetime.

Table 6. Direct Four-Electron Pathways and Catalysts[104,105]

Solutions	Reactions	Catalysts
Alkaline	• $O_2 = 2H_2O + 4e^- \rightarrow 4OH^-$ (0.401 V vs. SHE)	• Noble metal: Pt, Ag, Pd • Metal oxide: $CoIrO_3$, $NiIrO_3$, RhO_2, IrO_2 • Perovskite oxides $(ABO_3)^{1)}$: $LaNiO_3$, $La_{0.5}Sr_{0.5}CoO_3$ • Pyrochlore oxides $(A_2B_2O_7)^{2)}$: $Bi_2Ru_2O_7$ • Spinel oxides: $Bi_2Ru_2O_7$, Co_3O_4
Acidic	• $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (1.229 V vs. SHE)	• Noble metal: Pt, Ir, Rh, Ru, and Os • Mixture of noble metal (or oxide): Pt/Ir, Pt/IrO$_2$

1) General formula of Perovskite type oxides: their properties are varied depending on the nature of A and B
2) General formula of Pyrochlore type oxides: their properties are varied depending on the nature of A and B

Table 7. Two-electron Reduction Pathways and Catalysts[104,105]

Solutions	Reactions	Catalysts
Alkaline solution	• $O_2 = H_2O + 2e^- \rightarrow HO_2^- + OH^-$ (−0.065 V vs. SHE) • $HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ (0.867 V vs. SHE) • $2HO_2^- \rightarrow 2OH^- + O_2$	• Noble metal: Hg, Au • Carbon • Most transition metal oxides • Oxide covered metals
Acid solution	• $O2 = 2H^+ + 2e^- \rightarrow H_2O_2$ (0.67 V vs. SHE) • $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (1.77 V vs. SHE) • $H_2O_2 \rightarrow 2H_2O + O_2$	

As cost-effective alternatives to noble metals, investigation on noble metal oxides (e.g., RuO_2 or IrO_2) and transition metal oxides (e.g., $NiCo_2O_4$, spinel) have been on-going. Some transition metal oxides show good performance in oxygen evolution (particularly spinel) so far. Development of low-cost catalysts is going to be a key factor for the successful commercialization of Li-air battery.

In another example, concerning Co_3O_4/RGO catalyst, it has been observed that this catalyst does not act as a conventional one to lower the activation energy (or overpotential) via providing a higher-rate reaction path. Rather, it acts as a kind of 'promoter' to enhance surface transport (or mass transport) of Li_xO_2 species during cycling[90] and the ultimate effects are the same (i.e., reduction of overpotential).

Nanostructured Catalysts. The nano-sized catalyst's role in reducing discharge/charge overpotentials has been widely researched[107-111] (see also Table 4). It is based on very straightforward and intuitive reasoning that the specific catalyst activity increases as the surface area per gram of the catalyst increases, i.e., the smaller the size of the catalyst particle the greater the

catalyst activity. For non-aqueous Li-air cells, the á-MnO_2 nanowire catalysts have been discussed as one of the excellent low-cost catalyst candidates. Various nanostructured MnO_2 materials (e.g., nanocrystals, nanotubes, nanofiber, and dendritic clusters) are mixed with nano-sized carbon-based materials (e.g., carbon black, carbon foam, and graphite). Recent calculations and experiments have suggested that nano-structured substrates decorated with nano-sized catalysts are also very promising.[84,112,113] For example, if Pt-clusters are deposited onto a graphene support, the oxygen-reduction activity is observed to be much higher.[120] Therefore, there are good grounds for the implementation of carbon-based nanomaterials; e.g., carbon nanotubes and graphene as support materials [114-116] to accommodate a larger amount of Li oxide.[117,118] Regarding metal nanoparticles they are good candidates as well because their catalytic properties can be considerably higher than that of bulk metals. However, it has been suggested that when the sizes of catalyst particles are within the nanometer range, specific catalyst activity does not always follow the above rationale. Often the actual relation between specific catalyst activity and size is largely dependent on

the particular type of catalyst;[114,119-123] e.g., Pt particles were found to show maximal mass catalyst activity[124] when their size is ranging from 2 to 4 nm. Note that in the case of the Au catalyst, the particle size for maximum activity is smaller than that of Pt catalyst.[125-127]

4. DISCUSSION

In this section challenges related to non-aqueous and the hybrid Li-air cell are briefly discussed: These challenges are unique for each system for the development of catalyst.

4.1. Issues Regarding Organic Type Li-air Cells

As for non-aqueous Li-air cells, conceivable different chemical reactions are depicted in Fig. 8.[12,128-142] The reaction route producing Li_2O, compared to that of producing Li_2O_2, seems to be beneficial because a larger capacity is expected: However, it was found to increase irreversibility considerably. Other alternative reaction routes producing intermediate products are reported as well.[128,142-144] Most of all, organic electrolytes, Li salts (e.g., LiBOB), and binders (e.g., PVdF) are observed to react with superoxide (O_2^-), and to decompose during discharge.[145] During charge, the oxidation of decomposed electrolyte products is involved in CO_2[146] and H_2O production instead of O_2. In addition to reactions induced by superoxide (O_2^-), chemical reactions between Li_2O_2 (it is strongly nucleophilic like O_2^-) and solvent are very problematic because they can produce carbonate which will

ultimately limit the rechargeability of Li-air cells.[147] In short, problems associated with the scantiness of stable electrolytes[138,149] toward reduced oxygen species and discharge product is the single biggest hurdle to overcome before the non-aqueous cells can be commercialized,[138,139,141,148-152] not to mention the need for further catalyst study. Recent reports even argue that active catalyst material may not be a necessary component based on the kinetic overpoentials study.[153] Overall, these complex issues are hampering the development of appropriate catalysts for the air cathode of non-aqueous Li-air cells.

4.2. Issues Regarding Hybrid Type Li-air Cells

An outstanding difference between the hybrid and non-aqueous Li-air cells lies in the cell structures[53,133,134,-156] and, unlike non-aqueous Li-air cells, the hydrid Li-air cell's oxygen reduction reactions (ORR) at air cathode is well established, particularly in the case of Pt[157] and carbon surfaces in alkaline solution.[158,159] Chemical reactions at air cathode are critically dependent on the acid-base characteristics of aqueous electrolytes, i.e., acidic, neutral, or basic.[160] From the cycling data of hybrid Li-air cells (Figs 5, 6, and 7), the effects of Pt catalysts are eminent. The role of catalysts has been observed to be critical in the reduction of overpotential. However, this does not indicate that there are no technical issues to be tackled. On the contrary, there are numerous technical obstacles including the limited lifetime of catalysts due to dissolution of Co catalysts[161-163], the corrosion of Pt catalysts in alkaline electrolytes,[162]
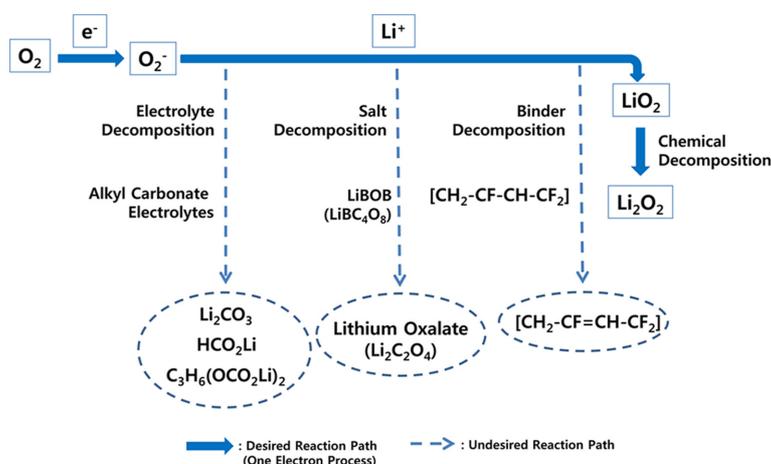

Fig. 8. Suggested Chemical Reactions During Discharge.12,128-142)

and the non-catalyst problems such as the instability of LiSICON in strong basic or alkaline electrolytes,[155,163] interfacial impedance increase due to insoluble phase formation,[164] electrolyte degradation (e.g., CO_2 in ambient air can react with alkaline electrolytes (LiOH, NaOH, and KOH) producing insoluble carbonate,[134] and Li dendrite formation[129,165] on the surface of Li metal. Finding a well matched pair of catalyst and aqueous electrolyte is still a hindrance in the development of hybrid Li-air cells, although it is not as deep a concern as is the case with non-aqueous Li-air cells. Most of all, the low-cost catalyst, which is alternating the expensive precious metal ones (e.g., Pt), is going to be one of the key factors in the commercialization of the Hybrid Li-air cell.

5. CONCLUDING REMARKS & PERSPECTIVES

The survey of previous research on catalysts clearly indicates that efforts have been primarily focused on the non-aqueous Li-air cell and its performance enhancement. The tendency toward more research of non-aqueous Li-air cells is based on the notion that these cells are expected to excel their hybrid counterparts in terms of gravimetric and volumetric energy density;[133] i.e., less numbers of components are required for the final cell assembly. However, appropriate heterogeneous catalysts for non-aqueous Li-air cells have not yet appeared. Difficulties in developing suitable catalysts stem from considerable complexity in relation to the analysis of Li-air cell's performance due to many involved parameters. These parameters, including pore structure of carbon support materials,[80,166,167] the choice of electrolytes (the viscosity, oxygen solubility, and ionic conductivity),[82,168,169] wettability between electrolyte and electrode,[167,170] binder, and the thickness of the electrode,[171] if not properly sorted out, will obscure catalysts' effects in the nano- and macro-scale. Thus, approaches for catalyst R&D should be multidisciplinary.[19,120,123,172] Regarding hybrid Li-air cells, there are also various parameters associated with cell performance, such as cathodic potential, oxygen purity, mass flow rate, cathode surface area, pH, and temperature.[159] However, this is a wholly different kind of challenge compared to that of non-aqueous Li-air cells as pointed out in the discussion section: No suitable electrolyte for non-aqueous Li-air cells has yet been discovered, and it is still a matter of controversy concerning the effects of catalysts due to undetermined ORR and OER mechanisms. The unavailability of reliable platforms is pertinent to the sluggish pace of catalyst development for non-aqueous Li-air batteries. In the case of hybrid Li-air cells, it is not uncommon to see that the current catalyst R&D is heavily resorted to the conventional catalysts developed (or being developed) for other metal-air batteries (or fuel cells): The control of morphology and orientation of crystal plane and its defect sites.[75,89,173-177] Still, in many cases platinum (Pt) is considered and adopted as the best catalyst,[176] although there are many reasons to devote research to developing cost-effective alternatives (e.g., perovskites, spinels, and pyrochlores[20] from the commercialization standpoint.

One of the prominent features regarding catalysts based on previous research is that all the catalysts are fabricated in nano-scale and nano-structure. Peculiarities in the microstructure of catalysts such as vacancies and defects are found to play a critically important role in determining the performance of Li-air batteries. Thus, inevitably there will be challenges related to the mass production of nano-structured catalysts, particularly in terms of controlling its crystal structure as required by specifications, i.e., morphology, defects, vacancies.[89] This perspective is based on the knowledge that nanomaterials are not always mass production friendly. However, despite these drawbacks, it is expected that nanomaterials will remain as a promising catalyst candidate for Li-air batteries, with the gradual maturity of related core technologies for upscale and mass production. In reality, for the commercialization success of Li-air batteries, simple and low cost catalyst production schemas should be devised.

6. ACKNOWLEDGEMENTS

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