Tuning Electrochemical Reactions in Li-O₂ Batteries

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Rechargeable lithium-O₂ battery is considered as promising next-generation devices for energy storage and conversion because of their high theoretical specific energy density. However, its application suffers from several issues such as high overpotential, poor cycle performance, and limited rate capability. Tuning electrochemical/chemical reactions in discharge and charge play an important role in reducing overpotential, increasing current density, and improving reversibility of Li-O₂ batteries. In this review, the fundamental principles and complicated electrochemical and chemical reactions in electrolytes and cathodes are first discussed. Based on these mechanisms, various strategies such as stabilizing electrode materials, selecting suitable electrolytes, adding catalysts and mediators, and changing O₂ pressure are reviewed to improve electrochemical performance by tuning electrochemical/chemical reactions. Finally, we explore future research directions in improving electrochemical performance of lithium-O₂ battery.

KEYWORDS: Lithium-O₂ battery; Electrochemical reaction; Charge/discharge process; Energy storage and conversion

I. Introduction

In the long term, society development’s need for energy storage such as electric vehicles (EVs) and large scale power station will far exceed that achievable by Li-ion batteries since the delivered energy and power densities of Li-ion batteries are not enough.¹–³ In contrast to conventional Li-ion batteries, non-aqueous aprotic Li-O₂ batteries can form Li₂O₂ in discharge by electrochemical and chemical reactions by Li⁺ and O₂, which induces an extremely large theoretical specific energy ~3500 Wh/kg and generate an equilibrium voltage of 2.96 V according to Nernst equation. In recent years, Li-O₂ batteries have received heightened attention because they can provide gravimetric energy density considerably higher than Li-ion batteries. However, to make Li-O₂ batteries suitable for practical applications, major challenges must be overcome, which include low round-trip efficiency, ⁴ ⁶–⁷ electrode and electrolyte instability,⁸–¹⁰ and low current density,¹¹–¹² and low cycle life.¹³–¹⁴

The electrochemical performance of Li-O₂ batteries is mainly regulated by the gas electrode (cathode), non-aqueous electrolyte, O₂ pressure, and additive catalysts and mediator in cathode or electrolyte.³ Li metal is currently used as anode to provide extra Li resource and ultimately will be replaced due to safety issue before and deployment of Li-O₂ batteries into real market. The cathode is a main site oxygen reduction reaction (ORR) during discharge and oxygen evolution reaction (OER) during charge. The solid-state catalysts are compositied on the cathode to enhance kinetic rate of ORR and OER.³ Therefore, the cathode should have a large surface area and large pore volume to store discharge product Li₂O₂, while catalyst contains enough active sites. Non-aqueous electrolyte not only functions as Li⁺ and O₂ diffusion channel, but also provides a site of electrochemical and chemical reactions in a molecule/ion level. During discharge, the O₂ released from oxygen reduction reaction on electrode reacts with Li⁺–complex to form superoxide (LiO₂⁻), further undergoing chemical disproportionation reaction to generate peroxy (LiO₂•). During charge, the Li⁺ and O₂ are continuously desorbed from Li₂O₂ surface and interface between Li₂O₂ and electrode (catalyst). Certainly, some metastable intermediates such as LiO₂ and Li₂O₄ may be generated.¹⁵–¹⁷ The above-mentioned electrochemical and chemical reactions are summarized as following:

Discharge Reactions:

\[ \text{O}_2 + (\text{Li}^+ + e^-) = \text{LiO}_2 \] (1)
\[ 2 \text{Li}_2\text{O}_2 = \text{Li}_2\text{O}_2 + \text{O}_2 \] (2)
\[ \text{Li}_2\text{O}_2 + \text{Li}^+ = \text{Li}_2\text{O}_4 \] (3)

Charge Reactions:

\[ \text{Li}_2\text{O}_2 = \text{Li}_2\text{O}_2 + (\text{Li}^+ + e^-) \] (4)

LiO$_2$ = O$_2$ + (Li$^+$ + e$^-$) \hspace{1cm} (5)

Although there is no general agreement on mechanism, it is sure that the complicated electrochemical and chemical reactions may occur on electrolyte and electrode. The deep discharge or strong ORR catalyst may result in the oxide Li$_2$O which is irreversible in electrochemical environment.\textsuperscript{18–19} The presence of O$_2$, O$_2^-$, Li$_2$O, and Li$_2$O$_2$ species and makes a practical Li-O$_2$ battery more complicated than expectation.\textsuperscript{20–21} They may lead to electrolyte and electrode decomposition during discharge. Some irreversible species such as Li$_2$CO$_3$ and Li$_2$C$_2$O$_4$ also may be produced by some side reactions.\textsuperscript{8–9}

It is of significant importance to tune these electrochemical and chemical reactions to avoid irreversible species to be formed and promote reversible and low-charge-potential species such as LiO$_2$/Li$_2$O. In this review, our discussion will concentrate on the main challenges of Li-O$_2$ batteries and how to improve battery performance by tuning electrochemical and chemical reactions.

2. Non-aqueous electrolytes

Although non-aqueous electrolytes have been studied and developed for decades and successfully applied in commercialized Li-ion batteries, they cannot be directly employed in Li-O$_2$ batteries. Electrolyte molecules coordinate with Li$^+$ ions and support fast Li$^+$ ion transport through the cells. This interaction has been demonstrated to be strongly related to cyclic performance of Li-ion and Li$_2$O batteries. In addition, the properties of formulated electrolytes are crucial to the interfacial structure between electrodes, O$_2$ gas, and electrolyte and accordingly regulate the performance of Li$_2$O$_2$ batteries. Very recently, some additives and mediators have been added into electrolyte to tune electrochemical and chemical reactions which are directly related to battery performance.\textsuperscript{22–26}

Because some highly oxidative intermediates are generated during discharge and charge of Li$_2$O$_2$ batteries, some possible polar organic compounds containing functional groups of carbonyl (C=O), nitrile (C≡N), sulfonyl (S=O), and ether (–O–).\textsuperscript{27} Based on these principles, the aprotic electrolytes such as carbonate, dimethyl sulfoxide (DMSO), phosphates, nitriles, and glymes have been attempted. In the following sections, we concentrate on the influence of electrolyte stability, additives and catalysts on electrochemical and chemical reactions in electrolyte in order to reveal the possible tuning mechanism in Li-O$_2$ batteries.

2.1 Electrolyte stability

As mentioned above, the oxygen reduction and evolution processes lead to the formation and decomposition of Li$_2$O$_2$ via a sequence of highly active intermediates such as O$_2^-$, LiO$_2$, O$_2^2-$, and LiO$_2^2-$\textsuperscript{20–21} The early attempts to operate Li$_2$O$_2$ batteries based on organic carbonate failed after few cycles as the overall process becomes dominated by electrolyte decomposition.\textsuperscript{28} Peter Bruce \textit{et al.} used mass spectrometry (MS) and in situ Surface Enhanced Raman Spectroscopy (SERS) techniques to measure Li$_2$CO$_3$, C$_6$H$_5$(OCO$_2$Li)$_2$, CH$_3$CO$_2$Li, HCO$_2$Li, CO$_2$, H$_2$O during discharge and charge.\textsuperscript{29} Several groups reported instability of carbonate electrolytes.\textsuperscript{30–32} More importantly, these generated species are irreversible in electrochemical processes and accumulate in the cathode on cycling, resulting in capacity fading and final cell failure. Such a failure indicates organic carbonates are not suitable as electrolyte of Li$_2$O$_2$ batteries. Luntz \textit{et al.} from IBM research group also observed CO$_2$ evolution from electrochemical reaction on carbonate electrolyte, while Dimethoxystyrene (DME)-electrolyte favours Li$_2$O$_2$ discharge product.\textsuperscript{10} T. Laino and A. Curioni performed molecular dynamic simulation (CPMD) to study decomposition mechanism of propylene carbonate under the presence of Li$_2$O$_2$ and Li$_2$O$_2$.\textsuperscript{20} They found that Li$_2$O$_2$ plays an important role in electrolyte decomposition rather than Li$_2$O$_2$.

In 2012, Jung \textit{et al.} found that glyme-based electrolyte may operate effectively to form many cycles with capacity and rate values as high as 5000 mAh/g and 3 A/g, respectively.\textsuperscript{33} Indeed, Ji-Guang Zhang \textit{et al.} also observed that a large amount of Li$_2$O$_2$ was generated in the air-electrode discharged in glyme-based electrolytes. DME was reported to be stable during cycling by McClosky \textit{et al.}\textsuperscript{10} Further, in situ quantitative gas-phase mass spectrometry and XRD confirmed Li$_2$O$_2$ was the main discharge product in the electrolyte of DME.\textsuperscript{34} However, the inconsistency between O$_2$ consumption and evolution amounts suggests there may exist a reaction between Li$_2$O$_2$ and DME. As shown in Figure 1, Li$_2$O$_2$ both decomposed to evolve oxygen and oxidized DME at high potential upon cell charge. At present, DME is still actively applied in Li-O$_2$ batteries.

![Figure 1 Gas evolution and current versus cell voltage during a 0.075 mV/s linear oxidative potential scan of a discharged DME-based cell. The cell was discharged at ~0.1 mA for 10 h under $^{18}$O$_2$ prior to the scan. Reproduced from Ref. 8 with permission of 2011 American Chemical Society.](image-url)
electrolyte and nonporous golden (NPG) or foam Ni as electrode have been applied in Li-O2 batteries. It was found that DMSO is stable within a voltage window from 2 to 4.35 V. The cycling performance showed dependence on the discharge depth and decayed with cycling. A higher charge potential leads to Li2CO3 and HCO3Li formation. Apart from AcN and DMSO, some other electrolytes such as NMP, triethyl phosphate, DMF, and methoxybenzene have been attempted. The reversible formation of Li2O2 could be observed in the initial few cycles, the capacity decayed quickly with cycling. Therefore, developing a stable electrolyte is still a long way in future.

Very recently, Peter Bruce et al. established electrolyte-dependent discharge product formation mechanisms, in solvent or on electrode surface. A unified mechanism of the pathway of O2 reduction to form Li2O2 called as solution pathway or electrode surface pathway was reported in their paper. They found the morphology of Li2O2 has been related to the solvent donor number (DN). In the intermediate-DN ethers, both electrode surface and solution pathway contribute significantly and simultaneously to Li2O2 formation at high voltages, leading to significant Li2O2 surface films and particles in solution. Low-DN solvents lead to Li2O2 film growth, decaying rate, low capacity and early cell death.

2.2 Solvating additive in electrolyte

Recently, several research groups found the trace amount of electrolyte additives such as H2O and acid can enhance the formation of Li2O2 toroids and result in significant improvement in capacity. Luntz et al. combined experimental measurements with theoretical modelling to study two different discharge mechanisms: one is surface electrochemical mechanism that produces conformal Li2O2 and the other is solution-mediated electrochemical process driven by Li2O2 partial solubility, where O2 acts as redox mediator and ultimately enhances the growth of Li2O2 toroids at low currents. Their studies strongly supported the second mechanism, as shown in Figure 2. The addition of water triggers the dissolution process of Li2O2 → Li (sol) + O2 (sol). These soluble O2 undergoes subsequent reaction on a growing Li2O2 toroid through the generic mechanism of 2 Li+ (sol) + 2 O2 (sol) = Li2O2 (s) + O2 (g). However, O2 is known to undergo disproportionation to form H2O2 which further performs a slow dissociation reaction. This step, along with a reaction between H2O and Li metal, slowly consumes the H2O and eventually this reduction of water reduces the overall dissolution rate of Li2O2 and ultimately terminates the solution growth mechanism. The similar reaction mechanism was also reported in Na-O2 batteries by Nazar’s research group.

Very recently, Zhou et al. developed a state-of-the-art Li-O2 battery in which ruthenium and manganese dioxide nanoparticles supported on carbon black super P (Ru/MnO2/SP) by applying a trace amount of water in electrolyte to catalyze the cathode reactions. They reported a charge potential of 3.5 V that 0.7 V higher than discharge potential, and superior cycling stability of 200 cycles. Further a new mechanism was proposed as conversion reaction of Li2O2 into LiOH catalyzed by trace amount of H2O2. Li2O2 + H2O = 2 LiOH + H2O2. The stable LiOH is MnO2-catalyzed to dissociate into H2O and O2. The resultant LiOH has a lower charge potential than Li2O2 due to a weaker electrostatic bonding between Li+ and OH-. Therefore, H2O plays an important role in converting Li2O2 into LiOH.

There are two possible catalysts added in Li-O2 batteries, solid-state catalyst on electrode surface and liquid-state redox mediator in electrolyte in order to reduce OER overpotential and improve cycling performance. The incorporated redox mediator (M) in electrolyte is oxidized directly at the electrode surface to generate M4+, followed by oxidizing the Li2O2 particles and reducing itself back to M. In essence, the redox mediator acts as an electro-hole transfer agent between electrode and Li2O2. The strategy is helpful to solve poor conductivity of Li2O2 and speed up kinetics of Li1O decomposition. In 2013, Peter Bruce et al. firstly studied tetrafluorinatedvulvalene (TFV) as a redox mediator, proving far more effective oxidation of Li2O2 as compared with its absence. The charge potential is reduced to
3.5 V with a complete reversibility of 100 cycles.

In 2014, Kang Kisuk et al. reported a Li-O₂ battery system using a soluble catalyst (LiI) combined with hierarchical nanoporous air electrode, achieving high reversibility and good energy efficiency. The cell can deliver a high reversible capacity (1000 mAh/g) up to 900 cycles with reduced charge potential of less than 3.5 V. Schematic illustration of the role of redox mediator in Li-O₂ battery are presented in Figure 3. Recently, Yunhui Huang et al. used the organic-electrolyte-dissolved iron phthalocyanine (FePc) as redox mediator to shuttle O₂⁻ species and electrons between Li₂O₂ and electrode, achieving an excellent electrochemical performance.

3. Cathodes

3.1 Metal and non-metal cathode materials

The solid Li₂O₂ formed on discharge must be stored a porous conducting matrix, which in practice has to combine sufficiently high conductivity and surface area with a low cost and ease of fabrication as a porous electrode materials. In addition, structural stability of electrode materials, especially with discharge and charge reactions, must be considered as a vital requirement. Carbon has extensively applied as cathode materials of Li-ion batteries due to its conductivity and large surface area. Several studies examined that carbon electrode appeared relatively stable. However, some side reactions were observed and attributed to carbon decomposition. Peter Bruce et al. studied carbon electrode using acid treatment and Fenton’s reagent by differential electrochemical mass spectroscopy (DEMS) and FTIR. As shown in Figure 4, they observed that carbon is relatively stable below 3.5 V on discharge and charge. Above 3.5 V, carbon may experience an oxidizing decomposition to form Li₂CO₃. But direct chemical reaction between carbon electrode and Li₂O₂ hardly take place during discharge and charge processes. However, discharged Li₂CO₃ was measured to have a relatively high charge potential, resulting in electrode passivation and capacity fading and irreversibility.

In 2012, Peng and Bruce et al. proposed a nanoporous gold and DMSO as air electrode and electrolyte, which generated excellent electrochemical performance with 95% capacity maintainence in 100 cycles. The electrode design with pure metal prevents carbon decomposition to block active sites of electrode. Following by this pioneering work, Wen et al.
designed a free-standing electrode of foam Ni nanocomposited with Co$_3$O$_4$ catalyst, which has a high discharge voltage of 2.95 V, a low charge voltage of 3.44 V, and high specific capacity of 4000 mAh/g, and low capacity fading. The electrode design principle and synthesized nanostructure are presented in Figure 5. They attributed these superior electrochemical performance to abundant available catalytic sites on electrode surface, the intimate contact of discharge product with the catalyst, the effective suppression of the volume expansion in the electrode during discharge and charge processes, the good adhesion of the catalyst to current collector, and the open pore system for unrestricted access of the reactant molecules to and from active sites of the catalysts.

Very recently, Larry Curtiss et al. constructed a nanocomposited electrode of iridium/reduced graphene oxide (Ir/RGO) and observed LiO$_2$ as alone discharge product, which was called as LiO$_2$ battery based on superoxide. This is different from their previous studies that Li$_2$O$_2$ and LiO$_2$ have been found with some different cathodes and electrolyte. They explained the existence of LiO$_2$ may be attributed to several possible factors. Firstly, Ir/RGO was used as electrode materials to favor fast deposition and crystal growth of LiO$_2$ due to a good lattice match between IrLi$_3$ and LiO$_2$, which is favorable to metastable LiO$_2$ growth. It indicates fast deposition of LiO$_2$ decreases soluble LiO$_2$ concentration and partially prevents disproportionation reaction into Li$_2$O$_2$. Without Ir incorporated into RGO, a different deposition and growth of discharge products may occur to lead to LiO$_2$ and Li$_2$O$_2$ mixture. Secondly, they attributed LiO$_2$ formation to O$_2$ desorption kinetics and interfacial effect between electrolyte and electrode. The ab initio molecular dynamic (AIMD) simulations indicated that O$_2$ had a lower desorption barrier from LiO$_2$ at the interface between LiO$_2$ and electrolyte, which greatly enhanced LiO$_2$ formation. Thirdly, a possible OER catalysis of Ir/RGO for Li$_2$O$_2$ dissociation into LiO$_2$ is not excluded. However, the complicated electrochemical and chemical reactions took place in solution and on electrode. By combining advanced experimental characterization techniques and quantum chemical computational methods, exploring these reaction mechanisms are very necessary to optimize electrochemical performance and design novel electrode materials of Li-O$_2$ batteries.

3.2 Solid-state catalysts

One of large challenges faced by Li-O$_2$ battery is the round-trip efficiency which is because of high overpotential or polarization of cathode reactions. A high charge voltage of 4.5 V and low discharge voltage of 2.7 V are measured, which leads to a low efficiency. An important strategy of improving this efficiency is applying effective catalysts on cathode. Although the previous experimental report by Luntz et al. doubted efficacy of electrocatalysis due to decomposition of carbonate electrolyte, a large amount of theoretical and experimental studies indicated that by applying electrocatalysts, discharge voltages could be increased and charge voltages could be decreased, which generated a higher round-trip efficiency with a longer cycling life and larger energy capacity. Therefore, we would review here several catalysts such as carbon, transition metal oxides, and noble metals.

Due to the controllable pore size, carbon materials have extensively applied as the air electrode of Li-O$_2$ batteries. Xia et al. synthesized mesocellular carbon material with narrow pore size distribution (30 nm) through nanocasting method by using nanosheets aggregated into loosely packed structures with large interconnected channels which are favorable to supply oxygen into the interior of the electrode using the discharge reactions. As shown in Figure 6, the structure can deliver the high energy...
In addition to the carbon porosity and structure, the carbon nature also affects the catalysis in Li$_2$O$_2$ battery. The N-doped carbon draws much attention because conjugation between lone-pair electron of N and graphene π-electron. The electronic properties play an important role in improving oxygen reaction activity. However, doping carbon materials used as oxygen evolution catalysts have not been reported in experiment. Ren et al. performed the first-principles thermodynamic calculations to study catalytic activity of X-doped graphene (X = B, N, Al, Si, and P) materials as potential cathodes to enhance charge reaction in Lithium-air battery. Among these materials, P-doped graphene exhibits the highest catalytic activity in reducing the charge voltage by 0.25 V, while B-doped graphene has the highest catalytic activity in decreasing the oxygen evolution barrier by 0.12 eV. By combing these two catalytic effects, B, P-codoped graphene was demonstrated to have an enhanced catalytic activity in reducing the O$_2$ evolution barrier by 0.70 eV and the charge voltage by 0.13 V. B-doped graphene interacts with Li$_2$O$_2$ by Li-sited adsorption in which the electron-withdrawing center can enhance charge transfer from Li$_2$O$_2$ to the substrate, facilitating reduction of O$_2$ evolution barrier. In contrast, X-doped graphene (X = N, Al, Si, and P) prefers O-sited adsorption toward Li$_2$O$_2$, forming a X–O$_2$$^-$–Li$^+$ interface structure between X–O$_2$$^-$ and rich Li$^+$ layer. The active structure of X–O$_2$$^-$ can weaken the surrounding Li–O$_2$ bonds and significantly reduce Li$^+$ desorption energy at the interface.

Tremendous research efforts in experiment and theory have been made to address high overpotential of charge reactions by incorporating transition metal compounds (TMC, oxide, carbide, nitride) in cathode to enhance OER kinetics. However, it is still controversial whether TMC can improve electrochemical performance of Li$_2$O$_2$ battery. Many TMCs were determined to have little, even not, catalytic effects in reducing overpotential and improving current density. In contrast, some transition metal oxide with novel nanostructures, doping metal, and conductive substrate were experimentally found to have catalytic activity for electrochemical reaction in Li$_2$O$_2$ battery. Among all applied metal oxides, spinel Co$_3$O$_4$ with a mixed oxidation states of Co$^{2+}$ and Co$^{3+}$ is promising as it can significantly reduce OER overpotential and improve cyclic performance of Li$_2$O$_2$ battery. After studying several metal oxides as cathode catalysts, Débart et al. found that Co$_3$O$_4$ supported on carbon gives the lowest charging voltage of ~4.0 V and maintains a relative good discharging capacity.\(^{5,7}\) In 2012, the electrochemical studies for an innovatively designed Co$_3$O$_4$@Ni cathode demonstrated a higher rechargeable capacity and much lower charging voltage (3.5 V) than noble metal Pt/Au as cathode catalyst. However, the detailed catalytic mechanism is unclear. Recently, Black et al. studied the electrochemical performance of Co$_3$O$_4$ grown on reduced graphene oxide (Co$_3$O$_4$@RGO) and observed kinetic improvement of mass transport for both OER and ORR.\(^{58}\) Zhu et al. performed first-principles calculation to elucidate that the O-rich Co$_3$O$_4$ (111) with a relatively low surface energy in high O$_2$ concentration has a high catalytic activity in reducing overpotential and O$_2$ desorption barrier due to the electron transfer from the Li$_2$O$_2$ to the underlying surface. Further they found that P-type doping of Co$_3$O$_4$ (111) exhibits significant catalysis in decreasing both charging overpotential and O$_2$ desorption barrier. Further Zhu et al. performed the first-principles calculations based on interfacial model were performed to study the OER mechanism of Li$_2$O$_2$ supported on active surfaces of TMC. They found that the O$_2$ evolution and Li$^+$ desorption energies show linear and volcano relationship with surface acidity of catalysts, respectively. Therefore, the charging voltage and desorption energies of Li$^+$ and O$_2$ over TMC could correlate with their corresponding surface acidity.

In 2011, Shao-Horn et al. reported the intrinsic oxygen reduction reaction (ORR) activity of polycrystalline Pd, Pt, Ru, Au, and glass carbon surfaces in 0.1 M LiCoO$_2$, 1, 2-dimethoxyethane via rotating disk electrode measurements. The Li$_2$-ORR activity of these surfaces primarily correlates to oxygen adsorption energy, generating a volcano-type trend. The activity trend found on the polycrystalline surfaces was in good agreement with the trend in the discharge voltage of Li$_2$O$_2$ cells catalyzed by nanoparticle catalysts. In comparison, Xu et al. calculated catalytic activity of Au, Ag, Pt, Pd, Ir, and Ru for catalyzing the Li-ORR.\(^{18}\) As shown in Figure 7, they predicted
Li-ORR has the smallest overpotential on Pt and Pd. The catalytic activity exhibits a volcano-like trend with respect to the adsorption energy of atomic O, which is in close agreement with the experimentally observed trend reported by Shao-Horn et al. 46

4. Conclusions and outlooks

The non-aqueous Li-O2 batteries have attracted a great deal of attention as potential energy-storage systems for future electric vehicle applications. However, it is still in developing stages and there are many technological problems to solve before becoming commercial applications. At present, controlling complicated electrochemical reaction processes and understanding these fundamental mechanisms become much important. Numerical systematic and detailed studies on materials and chemicals are still required to enhance discharge and charge reaction kinetics and regulate discharge products.

Several factors such as stability, catalytic activity, electronic and Li+ conductivity, and O2 diffusivity and adsorption must be considered in terms of designing novel electrode materials. In comparison, carbon electrode is relatively unstable because some reactions intermediates such as O2 and O22- can attack the defective carbon to form Li2CO3 which is irreversible and has a relatively high charge potential. Metal electrodes combining with catalysts may have good electric conductivity and stability. Therefore, the development of non-carbon-based supporting materials such as metal and metal oxides with novel nanostructure (nanowire, nanotube, and nanosheet) is of much importance for developing high-performance Li-O2 barriers.

Electrolyte plays an important role in regulating electrochemical reactions because the reduced O2 enters into electrolyte to combine with Li+. Some electrolytes such as carbonate are unstable with reactive intermediates, resulting in Li2CO3 formation to cover active electrode and capacity fading. Ethers and DMSO electrolytes were found to have a good electrochemical performance and expected to be extensively applied in future. Some additives such as H2O and liquid-catalyst are mixed with electrolyte to control electrochemical reactions. However, their tuning mechanisms are not very clear.

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Notes and references
