



Special Feature: Energy Conversion and Storage

Research Report

Solvent Screening and Capacity Enhancement of Li-air Battery with Radical Reactions

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■ABSTRACT■ Oxygen radical control has very important roles in Li-air battery and its development. One of the major issues of the battery stability is the decomposition of the solvent in the electrolyte because the oxygen radicals generated in discharge are very reactive against the solvents. We have developed a facile and effective method to explore the solvents using a radical generator, KO_2 . Ionic liquids and some solvents have been found to be possible solvents for the battery, and the performance of the batteries have also been actually demonstrated. By the use of the other aspect of the oxygen radical control, we have also developed a battery with extremely high capacity. The battery, Li- O_2 / CO_2 battery, uses an oxygen radical trapping reaction by CO_2 and has almost three times higher capacity than Li-air(O_2) battery. The main reason for the high capacity is attributed to the relatively slow precipitation of the discharge product, Li_2CO_3 . This new battery technology and the concept will open the door for an alternative energy source by providing CO_2 -rich gas such as exhaust gas from automobile or factory. The concept can also be easily extended to the other battery systems such as non-lithium systems.

■KEYWORDS■ Radical, Li-air, Battery, CO_2 , KO_2 , Screening

1. Introduction

For the development of electrified vehicles such as pure electric vehicle (PEV), plug-in hybrid vehicle (PHV) or hybrid vehicle (HV), the capacity enhancement of batteries is one of the key issues for the drastic improvement of the vehicles' performance. Next generation batteries beyond a typical Li-ion secondary battery are under development for those targets. The new concept, the combination between non-aqueous electrolyte and oxygen reducing reaction has opened a new research field for extremely large capacity battery, which is called a Li-air or Li- O_2 battery.⁽¹⁻³⁾ A theoretical calculation has predicted that the capacity reaches 11680 Wh/kg, the comparative value to the energy density of gasoline.⁽³⁾ Although the actual capacity by the laboratory experiment has shown much smaller value (<1700 Wh/kg), the battery still performs very large capacity as compared with the other battery systems.

One of the other features of Li-air battery is the generation of oxygen radical species in the discharging process. Many researches by far have revealed that the

radicals lead both beneficial and detrimental effect for the battery's performance.^(4,5) In this report, we also have focused on the control of the oxygen radical species and proposed that a new screening technology to develop the electrolyte of the Li-air battery using a radical generating compound⁽⁶⁾ and a new battery system based on Li-air battery using a radical trapping effect by CO_2 .⁽⁷⁾

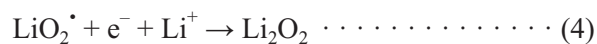
2. KO_2 Screening Technique for the Solvent of Li-air Battery

2.1 Overview of Solvent Screening Technique of Li-air Battery's Electrolyte Using KO_2

In the early stage of Li-air battery development, carbonate-based electrolytes, popular electrolytes of Li-ion battery, were used, and the batteries showed relatively high reversible discharge/charge performance.⁽¹⁾ However, careful investigation of the discharge product in the cathode and generated gases in charge process have revealed that the discharge process is totally different from the proposed reaction, a

reversible production of Li_2O_2 .⁽⁸⁻¹¹⁾ The actual discharge products are Li_2CO_3 and lithium alkyl carbonates, and generated gases are CO_2 , CO and so on.⁽⁸⁾ These facts have indicated that the discharge process is the decomposition of the solvents in the electrolyte, and the charge process decomposes again such decomposed species. Theoretical calculations have also supported the prediction.⁽¹²⁾ Then, it is necessary to explore new candidates of the solvents to establish a truly reversible Li-air battery system. One of the ordinary approaches to find the solvents is a traditional trial-and-error approach, which means the direct analysis of the each cathode to examine Li_2O_2 production using X-ray diffraction (XRD) or Raman spectroscopy technique after discharge applying many different kind of solvents. The approach is, however, not easy because the sensitivity of such compounds are generally low in the porous carbon structure which is normally used as the electrode material. Therefore, the non-electrochemical reproduction of the electrochemical reaction in the battery system is very useful to establish facile screening technique for the stable solvents.

In the Li-air battery, oxygen is reduced to form superoxide anion radical species, $\text{O}_2^{\cdot-}$, and the mechanism is a unique reaction in aprotic media (Eq. 1).⁽¹³⁾ The very reactive $\text{O}_2^{\cdot-}$ causes following chemical reactions to produce final discharge products in the actual Li-air battery. To simulate this reaction non-electrochemically, one need to generate $\text{O}_2^{\cdot-}$ in candidate solutions. We selected KO_2 as an $\text{O}_2^{\cdot-}$ generator for the screening. KO_2 is well known compound to generate $\text{O}_2^{\cdot-}$ for syntheses and analyses due to its dissociating property in aprotic media. If the expected reaction is allowed to occur in a candidate solvent in the presence of lithium ion, Li_2O_2 should be precipitated soon after the addition of KO_2 in the solution. The analysis of the precipitate has no difficulty because there is no other solid compounds such as electrode materials. In this non-electrochemical system, the Li_2O_2 forming reaction should be a disproportionation process of LiO_2^{\cdot} (Eqs. 1-3), and the reaction is different from the sequential two-step reduction (Eqs. 1, 2, 4), which may be included in the actual electrochemical reaction in the Li-air battery. However, the direct $\text{O}_2^{\cdot-}$ and/or LiO_2^{\cdot} detection in the real Li-air battery has also been reported,⁽¹⁴⁾ and the fact strongly supports the effectiveness of the non-electrochemical simulation by KO_2 .



2. 2 Experimental Procedure of KO_2 Screening

All following process and analysis were carried out under inert gas (Ar) atmosphere. Yellowish KO_2 powder (0.2 g, 2.8 mmol, Aldrich) was slowly added in 10 ml of a candidate solvent with/without 1 M of Li bis(trifluoromethanesulfonyl)imide (LiTFSI, Kanto Chemical Co.), and the solution in a bottle was placed 24 hours in room temperature. After the precipitation, the solid product was filtrated by separable syringe filter (1 μm pore) and washed in dimethylsulfoxide (DMSO) and chloroform three times, respectively. After drying in vacuum, the precipitate was analyzed by Raman and IR spectroscopy. Analytical method of Raman and IR were identical of our previous report.⁽⁷⁾ Baseline calibration of Raman spectra of the precipitates have been carried out for the results using trimethyl phosphate (TMP) and sulfolane (SULF) due to a large broad fluorescence peak.

2. 3 Results of KO_2 Screening Test

As mentioned above, one of the popular carbonate solvents, PC, has been found an unstable solvent for the Li-air systems,⁽⁸⁾ and we needed to clarify the capability of the KO_2 screening technique probing the instability of PC. KO_2 was added in PC with and without LiTFSI. There was almost no change after the addition of KO_2 in the absence of LiTFSI in PC even in the presence of 12-crown-4, a dissociation promoter of KO_2 to enhance $\text{O}_2^{\cdot-}$ concentration. The fact indicates that PC itself is almost stable against $\text{O}_2^{\cdot-}$. On the other hand, a rapid reaction including precipitation and gas generation was observed just after the addition of KO_2 in the presence of LiTFSI. Raman spectroscopy revealed that the white precipitate consisted of Li_2CO_3 , lithium alkyl carbonates and similar compounds, and gas chromatography indicated that oxygen was the main component of the generated gas. It is also important to note that Li_2O_2 nor Li_2O has been detected in the precipitate at all. From these observations, we can conclude that PC has been decomposed by the

reaction with highly reactive LiO_2^\cdot , the expected radical species only in the presence of Li^+ (Eq. 2). This speculation is consistent with the experimental report by Bruce's group⁽⁹⁾ and theoretical calculation by Bryantsev's group⁽¹²⁾. This result strongly supports that the KO_2 technique is effective to judge the stability against O_2^\cdot .

The other solvents have been applied the KO_2 screening test, and **Fig. 1** shows the Raman spectra of the precipitates collected from the solutions after the reaction with KO_2 in the presence of LiTFSI. The peaks at 261 and 791 cm^{-1} are attributed to Li_2O_2 , and the spectra of all precipitates except PC indicates the existence of the peroxide. Among all the candidate solvents in this experiment, ionic liquid (*N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide: PP13-TFSI, Kanto Chemical Co.) and acetonitrile (ACN) show very good stability by the Raman analysis. It is well known that specific kind of cation in ionic liquid, including PP13⁺, can stabilize O_2^\cdot by forming ionic-couple, and electrochemical reversibility of the oxygen anion was also confirmed and reported by Katayama's group.⁽¹⁵⁾ Recent report by Yamada's group has indicated that the possibility of the use of ACN-based electrolyte for the Li-air battery by the stabilization of ACN, normally highly reactive solvent against metallic Li, using highly concentrated solution of Li^+ .⁽¹⁶⁾ As indicated by the screening test, ionic liquid is one of the most stable solvents for the Li-air

battery systems, and we have already reported the actual battery performance using the ionic liquid based electrolytes.^(13,17-19) PP13-TFSI and *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium TFSI (DEME-TFSI) show relatively high coulombic efficiency and clear productivity of Li_2O_2 as a discharge product. The cross-sectional microscopic observation of the discharged cathode (air-electrode) has also indicated that the slight irreversibility is caused by undecomposed Li_2O_2 even after a charge process.⁽¹⁸⁾ It may be due to the electronic insulating effect between carbon support and Li_2O_2 in charging, and recent report has indicated such phenomenon.^(20,21)

In the cases of 3-methoxypropionitrile (MPN), DMSO and SULF (**Figs. 1, 2**), the decomposition of the solvents themselves have been relatively moderate, and the facts indicate the possibility of the application of these solvents to the Li-air systems. The actual battery performance using DMSO-based electrolyte and baseline-calibrated Raman spectrum of the cathode after discharge are shown in **Figs. 3a** and **3b**, respectively. The discharge-charge evaluation condition was identical of our previous report. The precipitation of Li_2O_2 (791 cm^{-1}) and relatively good electrochemical reversibility were also confirmed (two major peaks at 1350 and 1590 cm^{-1} are attributed to D- and G-band of carbon). A large broad peak in the Raman spectrum (Fig. 3b inset) will be attributed to fluorescence from small amount of decomposed

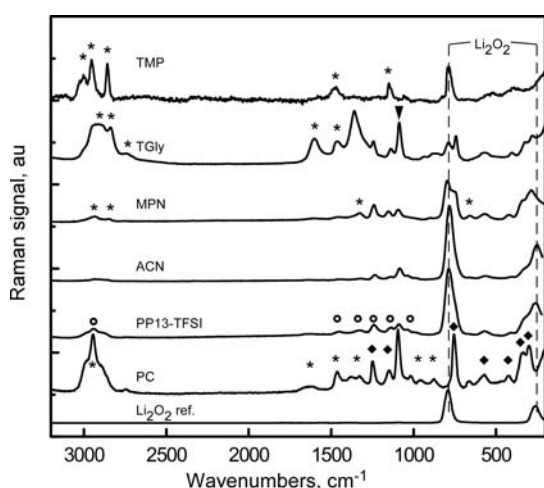


Fig. 1 Raman spectra of precipitates after the reaction in KO_2 screening tests except S-containing solvents (*: decomposed solvents, \circ : PP13-TFSI, filled diamond: LiTFSI, filled reverse triangle: Li_2CO_3).

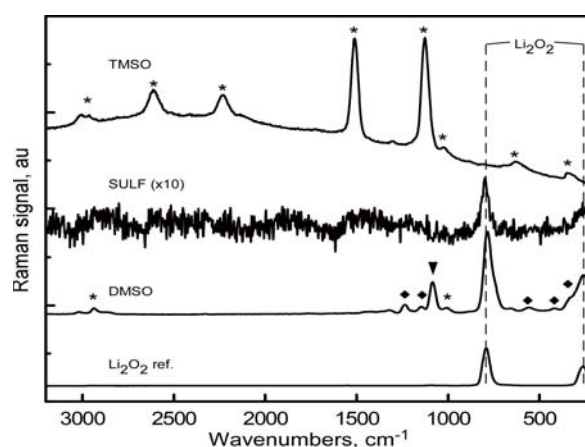


Fig. 2 Raman spectra of precipitates after the reaction in KO_2 screening tests for S-containing solvents (*: decomposed solvents, filled diamond: LiTFSI, filled reverse triangle: Li_2CO_3).

species of DMSO. These observations are consistent with the results of KO_2 screening test. Tetraglyme (TGly), TMP and tetramethyl sulfoxide (TMSO) have shown severe decomposition of themselves by the reaction with LiO_2^\cdot . Especially, TGly has been totally changed its molecular structure after the reaction from the observation by IR spectroscopy (Fig. 4). These solvents should not be applied to the Li-air battery systems.

From the above results and discussion, the effectiveness of KO_2 screening technique has been proved, and we have successfully demonstrated actual Li-air batteries using ionic liquid based and DMSO-based electrolytes. It is, however, worth to note that our method only confirms the short term stability

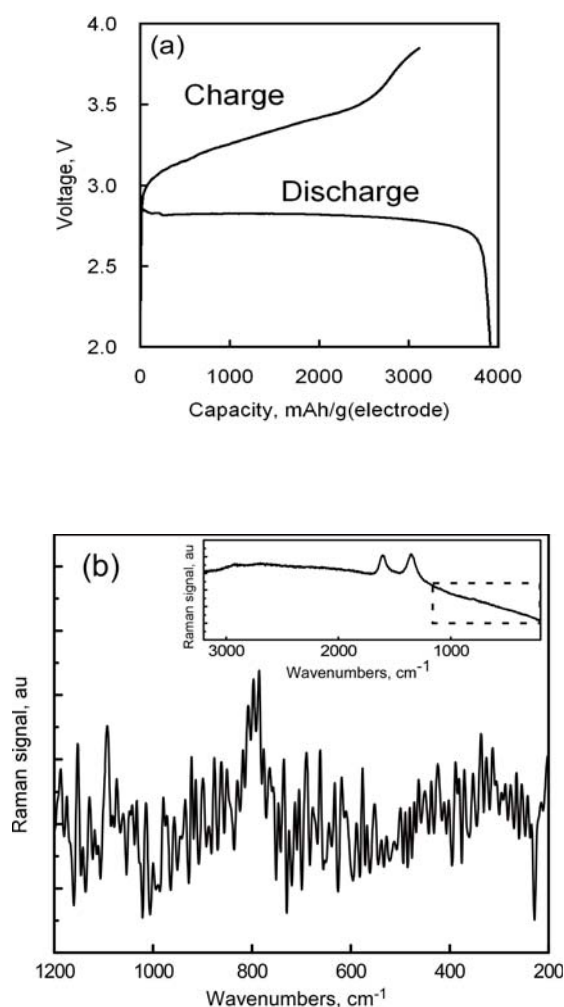


Fig. 3 (a) Discharge-charge behavior of Li-air battery and (b) baseline-calibrated Raman spectrum of the cathode after discharge using DMSO-based electrolyte. Inset of (b) shows whole Raman spectrum before baseline calibration.

of the solvents against oxygen radical species and does not guarantee all required properties of the solvent such as long term stability or the other possible side reactions.

3. Li- O_2 /CO $_2$ Battery

3.1 Overview of Li- O_2 /CO $_2$ Battery

One of the major features of the ordinary Li-air battery system is its extremely high capacity. Such high capacity is originated from the precipitation of high density discharge product, Li_2O_2 , in the air-electrode, which has large vacancy in its porous carbon structure.⁽³⁾ However, Li-air battery, which only consume oxygen in discharge, only performs the capacity far from its theoretical upper limit because the vacancy is difficult to be occupied by Li_2O_2 completely.⁽³⁾ As seen in **scheme 1**, oxygen radical species such as $\text{O}_2^{\cdot-}$ and LiO_2^\cdot have very important role in the Li-air battery system, and the reactivity of LiO_2^\cdot is very high as described in section 2. The capacity limitation may be caused by the rapid precipitation of insulating Li_2O_2 on the surface of the carbon support due to the high reactivity of LiO_2^\cdot . In other words, the control of the radical species will change the battery performance dramatically especially for its capacity.

Our strategy to improve the capacity is to trap oxygen radical species before forming Li_2O_2 (Eqs. 2-4) to realize slower precipitation in air-electrode. In this report, we selected CO_2 because it was well known that CO_2 had a good $\text{O}_2^{\cdot-}$ trapping property as described in the sequential Eqs. 5-8.⁽²²⁾ The property has also been

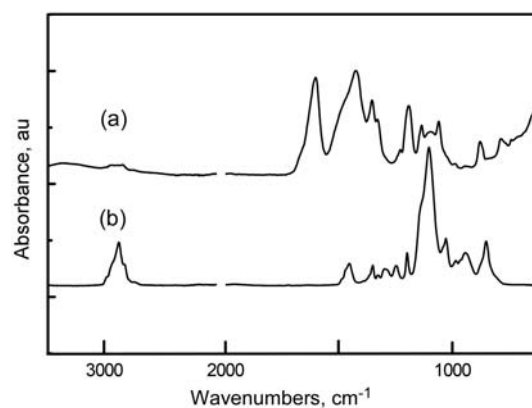
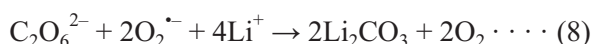
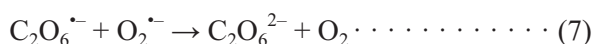
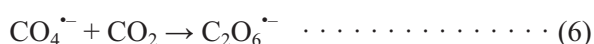


Fig. 4 IR spectra of (a) precipitate after KO_2 test in TGly and (b) TGly itself.

used in CO₂ sensors or molten-carbonate fuel cell (MCFC).^(22,23) To allow the reactions, one need to introduce both O₂ and CO₂ at the same time, and we call the new battery system, a Li-O₂/CO₂ battery. Aurbach's group has already proved the electrochemical stability of Li metal, a typical anode active material of Li-air battery, in the presence of CO₂ in a moderate temperature range and the introduction of CO₂ is rather suitable for lithium batteries because of the protecting effect on the surface of Li metal by Li₂CO₃ thin film.^(24,25)



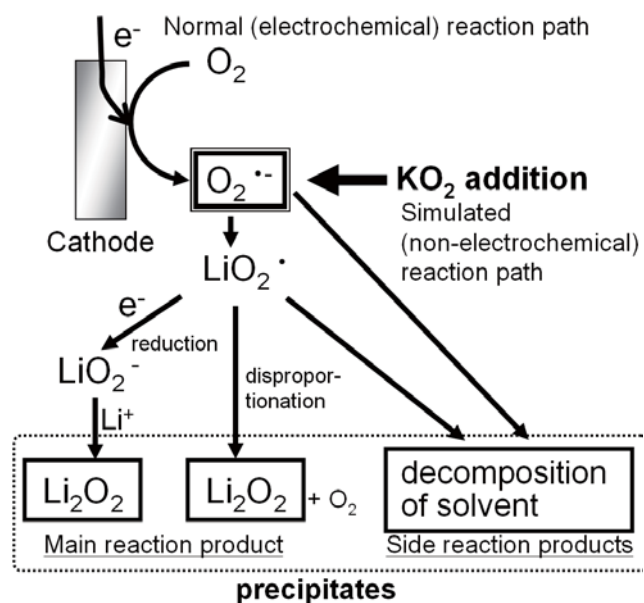
3.2 Fabrication of Li-O₂/CO₂ Battery

The basic structure of the cell and electrodes are identical to those of the Li-O₂ battery, and Swagelok type cells were used in evaluating the Li-O₂(/CO₂) batteries in this study.⁽¹⁾ A sheet type electrode with a thickness of 80 μm consisting of Ketjen-black

(90 wt%) and PTFE binder (10 wt%) was used as the cathode. Li foil and a solution of 1M LiTFSI in the mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (3:7 vol.) were used as an anode and an electrolyte, respectively. The mixed gas of O₂ and CO₂ was introduced into the cell directly using 50 ml cylinder with a pressure of 2 kgf/cm². All discharge measurements were carried out at 25°C.

3.3 Performance of Li-O₂/CO₂ Battery

Figure 5 shows discharge profiles of Li-O₂, Li-CO₂ and Li-O₂/CO₂ batteries. The difference among these batteries are only gases introduced in the battery cells, 100% O₂, 100% CO₂ and the mixture of 50% O₂ and 50% CO₂, respectively. The discharge capacity of the Li-O₂ and Li-CO₂ batteries were 3068 and 82 mAh/g with the current density of 0.1 mA/cm², respectively. Such low discharge capacity of Li-CO₂ battery is caused by the higher cut-off voltage, 1.5 V, than the direct reduction potential of CO₂, around 1.4 V (vs Li/Li⁺),⁽²¹⁾ and it indicates that the battery only has poor theoretical energy density. In the case of Li-O₂/CO₂ battery, the discharge capacity was 6750 mAh/g and 220% as compared with that of the Li-O₂ battery. The almost same plateau voltage in discharge as compared with Li-O₂ battery, around 2.7 V, implies that the reduced species is O₂ in the both cases. Figure 6 shows the performances of Li-O₂/CO₂



Scheme 1 Normal and simulated reaction paths of KO₂ screening test for the solvent of Li-air battery.

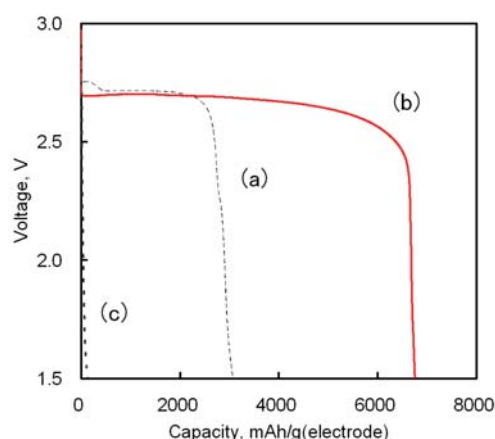


Fig. 5 Discharge curves of the Li-O₂/CO₂ batteries with various ratio of CO₂ in O₂/CO₂ mixed gas at 25°C (current density: 0.2 mA/cm²). Inset shows CO₂ ratio dependence on relative capacities as compared with the Li-O₂ battery (CO₂ 0%).

batteries with different gas ratio between O_2 and CO_2 (current density: 0.2 mA/cm^2). As indicated in the inset of Fig. 6, the relative capacity compared with $Li-O_2$ battery has been largely increased from only 10% of CO_2 mixture in the gas and reached almost three times in the range from 30 to 70% of CO_2 ratio. Higher than 70% of CO_2 ratio, the capacity has been dropped dramatically due to the lack of O_2 , the electron acceptor.

To elucidate the mechanism for the extreme high capacity, we observed inner structure of air-electrodes by FIB-SEM technique. The cross-section images before and after discharge, which were washed with DEC thoroughly, are shown in Fig. 7. They clearly show that the void volume of the electrode after discharge is totally occupied with the product of discharge reaction. In general, the occupation ratio of the void volume by the discharge product is far from 100% for $Li-O_2$ battery even under low current density.^(8,26) For instance, the ratio is only around 50% in the case $Li-O_2$ battery with ionic liquid based electrolyte.⁽¹⁸⁾ These facts indicate that the $Li-O_2/CO_2$ battery has another storage mechanism to perform such high capacity.

The chemical components of the discharge product of $Li-O_2/CO_2$ battery was analyzed by IR spectroscopy (Fig. 8). The spectrum clearly shows that the product is Li_2CO_3 , while the expected products in $Li-O_2$ battery, Li_2O_2 or Li_2O , are not detected at all (small amount of LiTFSI is also detected as a residue of the

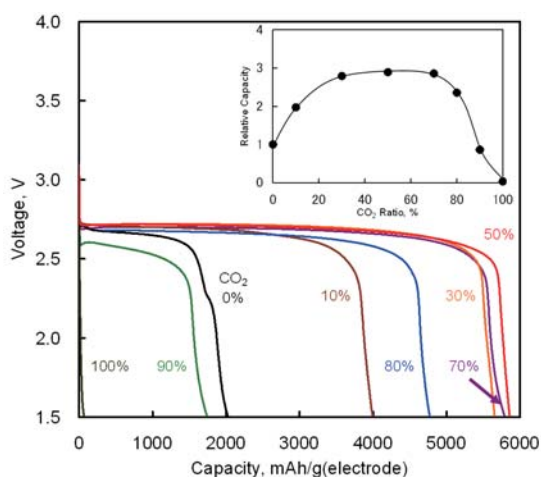


Fig. 6 Discharge curves of the $Li-O_2/CO_2$ batteries with (a) 0, (b) 50, and (c) 100% of CO_2 in O_2/CO_2 mixed gas at $25^\circ C$ (current density: 0.1 mA/cm^2).

supporting electrolyte). It is important to note that the presumed intermittent species, peroxydicarbonate ion ($C_2O_6^{2-}$) (Eq. 7), is not detected,⁽²³⁾ and the fact means that the peroxydicarbonate ion is a highly reactive species even it existed in the system temporally. The total weight gain of the air-electrode after discharge is 25% larger than that of theoretical mass of Li_2CO_3 produced by two-electron electrochemical reaction calculated by the actual discharge capacity. Since the IR spectrum of the discharge electrode indicates the existence of LiTFSI (Fig. 8), co-precipitation of Li_2CO_3 and LiTFSI is highly possible.

To understand the mechanism of the high discharge capacity of $Li-O_2/CO_2$ battery, kinetic comparison among proposed multiple reactions is essential. The first step of the reactions is the same process in both $Li-O_2$ and $Li-O_2/CO_2$ batteries because the discharge

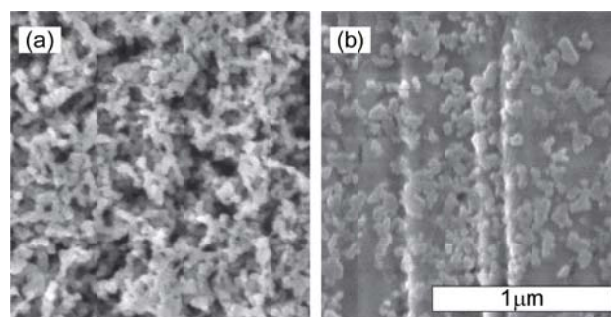


Fig. 7 Cross-section SEM images of the cathode of the $Li-O_2/CO_2$ battery (a) before and (b) after discharge ($O_2:CO_2 = 1:1$, current density: 0.1 mA/cm^2).

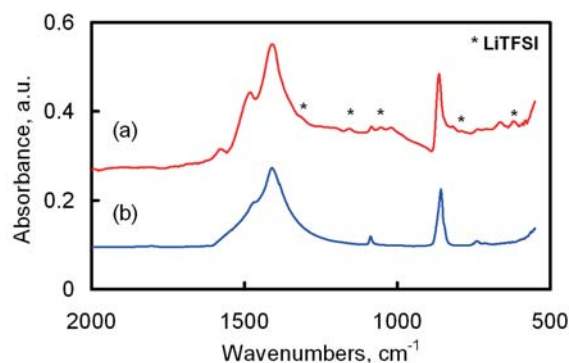


Fig. 8 IR Spectra of (a) the cathode of discharged $Li-O_2/CO_2$ battery and (b) standard Li_2CO_3 .

voltage in both batteries are identical and determined by the same oxygen reduction (Eq. 1). The second step, however, must be different. In the case of Li-O₂/CO₂ battery, the O₂^{•-} trapping reaction by CO₂ (Eq. 5) is dominant to the LiO₂[•] forming reaction usually seen in Li-O₂ battery (Eq. 2). If the reaction, Eq. 2, is also allowed to occur in the presence of CO₂, the only way to produce Li₂CO₃ is the reaction between Li₂O₂ and CO₂ (Eq. 9) AFTER the precipitation of Li₂O₂ on the surface of the air-electrode. This hypothesis can be ruled out because the mechanism cannot explain the complete filling effect of the void volume in the electrode.



Therefore, the reactions, Eqs. 5-8, are inevitable in Li-O₂/CO₂ battery. We assume that one of the intermittent species in Eqs. 5-8, such as peroxydicarbonate ion (C₂O₆²⁻) for example, is a relatively long-lived species to be diffused in the pore of the electrode (and will disappear completely by following reactions), and helps the complete filling by the final product, Li₂CO₃. The discharge capacity of the Li-O₂/CO₂ battery is effected by the current density (Figs. 4, 5) even with the same CO₂ ratio, and the variation may be caused by uneven precipitation in higher current density on account of increased concentration of intermittent species. We are still running the project to elucidate the mechanism and properties of Li-O₂/CO₂ battery and believe that the performance of the battery is improved further for the future application.

4. Concluding Remarks

Recent aggressive research activities of the Li-air battery technology have revealed that oxygen radical species, such as O₂^{•-} and LiO₂[•], are very unique and have important roles in the system. Therefore, the smart control of the radicals opens the way to improve the battery's stability and capacity. In this report, we proposed two different approaches for Li-air battery development by the use the radical control techniques.

In the first approach, KO₂ is used as an oxygen radical donor to establish a non-electrochemical reactivity test to explore stable solvents for the electrolyte of the battery. The simple and facile technique is very effective to simulate the discharge reaction and provides clear indications for the stable solvents. Ionic liquids and DMSO, the suggested

solvents by the screening test, actually have performed stable discharge/charge cycles and demonstrated the effectiveness of the test. We believe that this technique will largely contribute the development of the Li-air battery.

In the second approach, we proposed the new gas-utilizing battery, the Li-O₂/CO₂ battery, using the mixed gas of O₂ and CO₂, which has extremely high discharge capacity. The O₂^{•-} trapping strategy by CO₂ is the main concept of the battery, and the slow filling effect of the void volume in air-electrode may help to enhance the discharge capacity drastically. Since the final discharge product is an electrochemically stable compound, Li₂CO₃, this battery cannot be charged again. However, the extraordinary high capacity, three times larger than Li-air (O₂) battery, will open the door for an alternative energy source by providing CO₂-rich gas such as an exhaust gas from automobile or factory. The concept can be easily extended to the other battery systems such as non-lithium systems, and some attempts have been done successfully and reported.⁽²⁷⁾

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Figs. 1-4 and Scheme 1

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Figs. 5-8

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