



Reaction mechanisms for the limited reversibility of Li–O₂ chemistry in organic carbonate electrolytes

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ABSTRACT

The Li–O₂ chemistry in nonaqueous liquid carbonate electrolytes and the underlying reason for its limited reversibility was systematically investigated. X-ray diffraction data showed that regardless of discharge depth lithium alkylcarbonates (lithium propylenedicarbonate (LPDC), or lithium ethylenedicarbonate (LEDC), with other related derivatives) and lithium carbonate (Li₂CO₃) are constantly the main discharge products, while lithium peroxide (Li₂O₂) or lithium oxide (Li₂O) is hardly detected. These lithium alkylcarbonates are generated from the reductive decomposition of the corresponding carbonate solvents initiated by the attack of superoxide radical anions. More significantly, *in situ* gas chromatography/mass spectroscopy analysis revealed that Li₂CO₃ and Li₂O cannot be oxidized even when charged to 4.6 V vs. Li/Li⁺, while LPDC, LEDC and Li₂O₂ are readily oxidized, with CO₂ and CO released from LPDC and LEDC and O₂ evolved from Li₂O₂. Therefore, the apparent reversibility of Li–O₂ chemistry in an organic carbonate-based electrolyte is actually an unsustainable process that consists of (1) the formation of lithium alkylcarbonates through the reductive decomposition of carbonate solvents during discharging and (2) the subsequent oxidation of these same alkylcarbonates during charging. Therefore, a stable electrolyte that does not lead to an irreversible by-product formation during discharging and charging is necessary for truly rechargeable Li–O₂ batteries.

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1. Introduction

With Li-ion batteries making their debut in the new generation of electric vehicles (EV) represented by the Nissan Leaf and the Chevrolet Volt, the developers of future EVs are envisioning battery systems that can provide energy densities well beyond what can be offered by state-of-the-art Li-ion technology (120 Wh Kg⁻¹~200 Wh Kg⁻¹). Although incremental improvements can still be achieved in Li-ion systems with new cathode materials that exhibit high specific capacities (e.g., greater than 200 mAh g⁻¹ or even 300 mAh g⁻¹) or high voltages (e.g., 5 V and above) and new anode materials with high specific capacities (e.g., silicon, tin and others), significant increases in specific energies will be needed to achieve the proposed 500 mile driving ranges

of future EVs. This reality has forced researchers to look beyond Li-ion systems for solutions, among which are Li–air and Li–sulfur systems.

Li–air or Li–O₂ batteries have ultra-high theoretical specific energies of approximately 11 kWh kg⁻¹ based on the lithium electrode alone, or about 5.2 kWh kg⁻¹ when the oxygen weight is included [1–3]. On system level a practical specific energy of 362 Wh kg⁻¹ with a nonaqueous electrolyte in pouch configuration has been achieved by Zhang et al. [4]. However, the reversibility of such a chemistry is still far from being satisfactory, with a cycle life ranging from several to 100 cycles depending on catalyst and electrolyte compositions [5–13], where, based on the success in Li-ion systems, organic carbonate esters were used as the primary electrolyte solvents. For example, Bruce and co-workers [7–9] reported that a Super S carbon electrode with electrolytic MnO₂ as the catalyst had an initial discharge capacity of 1000 mAh g⁻¹ (based on the weight of carbon) at a current rate of 70 mA g⁻¹ and a capacity retention of 60% after 50 cycles, while Mizuno et al. [12] reported that a Super P (SP) carbon electrode with MnO₂ powder as a catalyst in a PC electrolyte had an initial discharge capacity of 820 mAh g⁻¹ and a 60% capacity retention after 100 cycles, which is the longest cycle life ever reported. The limited cycle life of the Li–O₂ chem-

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istry in carbonate-based electrolytes was thought to be caused by the discharge products, which are primarily carbonate species from the reduction of solvent molecules (lithium carbonate (Li_2CO_3) and lithium alkylcarbonate) rather than the desired lithium peroxide (Li_2O_2) [12]. The formation of these carbonate species has been hypothesized to be based on the reaction of Li_2O_2 with either PC or CO_2 gas in the presence of trace moisture, or the decomposition of the PC solvent through reactions with the O_2 radicals or superoxide anions that are formed during the initial O_2 reduction. The presence of carbonate species in Li–air systems has been confirmed with both Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) [12,14].

More recently, we also reported the application of *in situ* gas chromatography/mass spectroscopy (GC/MS) to gas evolution analysis during the charging process of a Li– O_2 battery using a Li_2O_2 -based electrode in an organic carbonate electrolyte [15]. We confirmed that Li_2O_2 can be oxidized to release O_2 with a high conversion yield, which is in agreement with results reported by Bruce and co-workers [7]. However, re-charging of an air electrode that was previously discharged in the carbonate-based electrolyte released CO_2 and CO, instead of O_2 [15]. Because XRD and FTIR analyses of discharged air electrodes have indicated that the discharged products were mainly organic and inorganic carbonate species, and the presence of Li_2O_2 is negligible [12,14,15], oxidation of Li_2O_2 thus becomes irrelevant, and it is of critical significance to understand whether these organic and inorganic carbonate species are re-oxidizable and whether their chemical properties impact the cyclability of the Li– O_2 chemistry in the corresponding carbonate electrolytes.

In this paper, we address this topic by systematically analyzing and identifying the discharged products on the cycled carbon air electrodes from Li– O_2 batteries in an organic carbonate electrolyte. Then, using synthesized model compounds as references, we examined the re-oxidizability of these discharge products in correlation to the reversibility of the proposed Li– O_2 chemistry in carbonate-based electrolytes. Our ultimate goal is to propose a possible discharge/charge mechanism that accounts for the low efficiency and poor cycle life observed in secondary Li– O_2 batteries that use nonaqueous carbonate electrolytes, which serve as guideline to the choice of electrolyte components for future Li– O_2 chemistry with better reversibility.

2. Experimental

2.1. Preparation of air electrodes and assembly of Li– O_2 coin cells

Li_2O_2 (technical grade, 90%), lithium oxide (Li_2O) ($\geq 99.8\%$ trace metal basis), Li_2CO_3 (A.C.S. reagent, 99+%), Fe_3O_4 (nanopowder, < 50 nm particle size, $\geq 98\%$ trace metal basis), 1-methyl-2-pyrrolidinone (NMP, spectrophotometric grade, 99+%), and 4 Å molecular sieves were ordered from Sigma–Aldrich. SP carbon black (from Timcal) and polyvinylidene fluoride (PVDF, from Arkema) were provided free by the manufacturers. A Ni foam sheet (density 380 g m^{-2} , 1.7-mm thick) was obtained from INCO Special Products. Lithium foil (99.9%, 0.75-mm thick) was purchased from Alfa Aesar. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), EC, PC, and dimethyl carbonate (DMC) (all in battery grade) were purchased from Novolyte Technologies. NMP was dried with 4 Å molecular sieves for a week before use; prior to that, the molecular sieves were activated at 300°C overnight. All other chemicals were used as received. LEDC and LPDC were synthesized as described in the literature [16].

In this work, in order to get enough discharged products for XRD analysis, high surface area carbon, i.e. Ketjen black (KB) carbon,

was used. The KB-based air electrodes were prepared as described in the literature [17]. DuPont Teflon PTFE-TE3859 fluoropolymer resin was used as a binder, and the weight ratio of carbon/Teflon after drying was 85:15. The KB carbon/Teflon powder was pressed into a self-standing sheet and then laminated onto a nickel mesh with the carbon loading in the final electrode being controlled at about 15.1 mg cm^{-2} . The KB air electrode disks had a diameter of 1.59 cm and an area of 1.98 cm^2 .

As for the studies on chargeability and cyclability of different potential discharged products (Li_2O_2 , Li_2O , Li_2CO_3 , LEDC and LPDC), modeling electrodes were designed to investigate the chargeability of the individual discharge products. Only one discharged product was used in one charge electrode sample to avoid the confusion caused by multi-components. Non-active materials, such as low surface area carbon (i.e. SP carbon) and nonaqueous-based binder system (i.e. PVDF in NMP solution) were used for easier handling, less solvent utilization and no decomposition of the active material by water. The SP air electrodes preloaded with Li_2O_2 , Li_2O , Li_2CO_3 , LEDC and LPDC as active agents with and without Fe_3O_4 were prepared inside an MBraun glove box filled with ultra-high purified argon where the moisture and oxygen content was less than 1 ppm. For air electrodes that did not contain Fe_3O_4 as a catalyst, a mixture of lithium oxide or salt as active agent and SP at a weight ratio of 1:1 was prepared. For air electrodes with Fe_3O_4 as a catalyst to lower the overvoltage of Li– O_2 batteries during charge process as reported by Bruce and co-workers [8], a mixture of lithium oxide or salt, SP, and Fe_3O_4 at a weight ratio of 39.4:51.3:9.3 was used as in our previous work [15]. Each solid mixture was ball-milled for 30 min in a high energy Spex SamplePrep 8000 M Mixer/Mill. Then, slurries of the ball-milled solid mixture and PVDF in NMP solution were separately coated onto Ni foam disks that were 1.59 cm in diameter and 1.98 cm^2 in area. After the NMP was evaporated in the antechamber of the glove box under vacuum, the air electrodes were further dried at 80°C under vacuum overnight. The weight ratio of the active material/SP/PVDF was set as 4:4:2, or active material/SP/ Fe_3O_4 /PVDF at 36.8:48.0:8.7:6.5. As a baseline comparison, the air electrodes of SP/PVDF at 8:2 by weight and SP/ Fe_3O_4 /PVDF at 84.8:8.7:6.5 by weight were also prepared.

The coin-cell-type Li– O_2 batteries of 2325 size were assembled inside the MBraun glove box as described in previously published papers [3,18]. The 2325 coin cell kits were purchased from Canada National Research Council (CNRC), and the cell pans were machine-drilled with $19 \times \text{Ø}1.0$ mm holes in an evenly distributed pattern for oxygen access. The cells were constructed by placing an air electrode disk on the cell pan, covering it with a piece of separator (2.06-cm diameter, Whatman® GF/D glass microfibre filter paper), adding excessive (about 280 μL) electrolyte (1.0 M LiTFSI in PC:EC at a 1:1 weight ratio), placing a 1.59-cm-diameter lithium disk, placing a 0.5-mm-thick stainless steel spacer with from Pred Materials, and finishing with a coin cell cover with a polypropylene gasket. The whole assembly was crimped at a gas pressure of 200 psi on a pneumatic coin cell crimper purchased from CNRC, and excessive electrolyte was expelled from the cells through the O_2 diffusion windows during crimping.

2.2. Test and characterization

Performance of the Li– O_2 coin-cell batteries was tested at room temperature on an Arbin BT-2000 battery tester. Each cell was placed in an individual 226-cm³ Teflon container filled with purified oxygen at a pressure slightly above 1 atm. Fig. 1 is a schematic of our experimental set up. Discharge of the KB air electrode was conducted at a current density of 0.05 mA cm^{-2} , and the depths of discharge (DOD) was varied by using different cutoff voltages of 2.8 V, 2.7 V, 2.6 V, 2.5 V, 2.4 V, 2.2 V and 2.0 V, respectively. When the set discharge voltage was reached, discharging was contin-

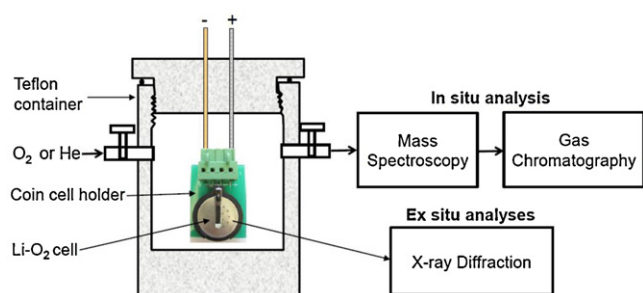


Fig. 1. The schematic of the experimental setup.

ued under the constant voltage process until the current density decreased to $\leq 0.01 \text{ mA cm}^{-2}$. For the rechargeability test of SP-based air-electrodes pre-loaded with lithium salt active species, the cells were cycled between 4.5 or 4.6 V and 2.0 V after charging.

Analysis of gas evolution of SP-based air electrodes during charging was conducted as described in a previously published report [15]. Each cell was placed in a 226-cm³ Teflon container, and the container was sealed tightly, with all processes handled inside the argon-filled glove box. The Teflon container with the cell was removed from the glove box and connected to a GC/MS instrument. The Teflon container was evacuated and refilled with purified helium at a flow rate of 50 cm³ min⁻¹. The evacuation and refilling cycle was conducted three times, followed by purging the container with helium for several hours at a flow rate of 3 cm³ min⁻¹. The cell was charged from the open circuit potential to 4.6 V at a constant current of 70 mA g⁻¹ based on the active material (e.g. Li₂CO₃) on a CHI 660C electrochemical workstation. The gases generated were analyzed in real time using GC/MS.

To analyze the air electrodes after discharging, the Li–O₂ coin cells were disassembled in the glove box. The air electrodes were washed thoroughly several times by immersion in fresh anhydrous DMC for at least 1 h each time, followed by drying under vacuum at room temperature overnight.

XRD patterns of the discharged air electrodes in powder state were measured in a D8 Advance X-ray diffractometer (Bruker AXS, Inc., Madison, Wisconsin) equipped with a HTK 1200 atmosphere-controlled chamber (Anton Paar, Ashland, Virginia) and a Vantec-1 position sensitive X-ray detector (Bruker AXS). Measurements were performed at room temperature under N₂ gas from 10° to 80° 2θ with 0.007° 2θ steps and at least 320.8 s of total count time per step. The measurement of XRD patterns of Li₂O₂ samples after reacting with PC or EC were made on a Philips Xpert X-ray diffractometer with Cu Kα radiation at λ1.54 Å, from 10° to 80° at a scanning rate of 0.02° per 10 s.

3. Results and discussion

3.1. Reductive processes during discharge

Fig. 2(a) shows XRD patterns of KB air electrodes at different DODs in an oxygen atmosphere, compared with a series of compounds serving as standard references (Fig. 2(b) and (c)), which include Li₂CO₃, Li₂O₂, Li₂O, synthesized lithium alkylcarbonates (LEDC and LPDC) that were known reduction species from EC and PC via single-electron pathway (Fig. 2(b)), pure KB carbon powder, Teflon powder, and KB-Teflon air electrode (Fig. 2(c)). It is clearly seen that for all the DODs (from 2.8 V to 2.0 V) lithium alkylcarbonates (LPDC and LEDC) and Li₂CO₃ are identified to be the primary discharge products, with barely any Li₂O₂ and Li₂O detected by XRD. This finding is in good agreement with previously published results [12,14,15]. By lowering the DOD from 2.8 V down to 2.2 V a decrease of crystallinity is observed. The KB carbon and the reduc-

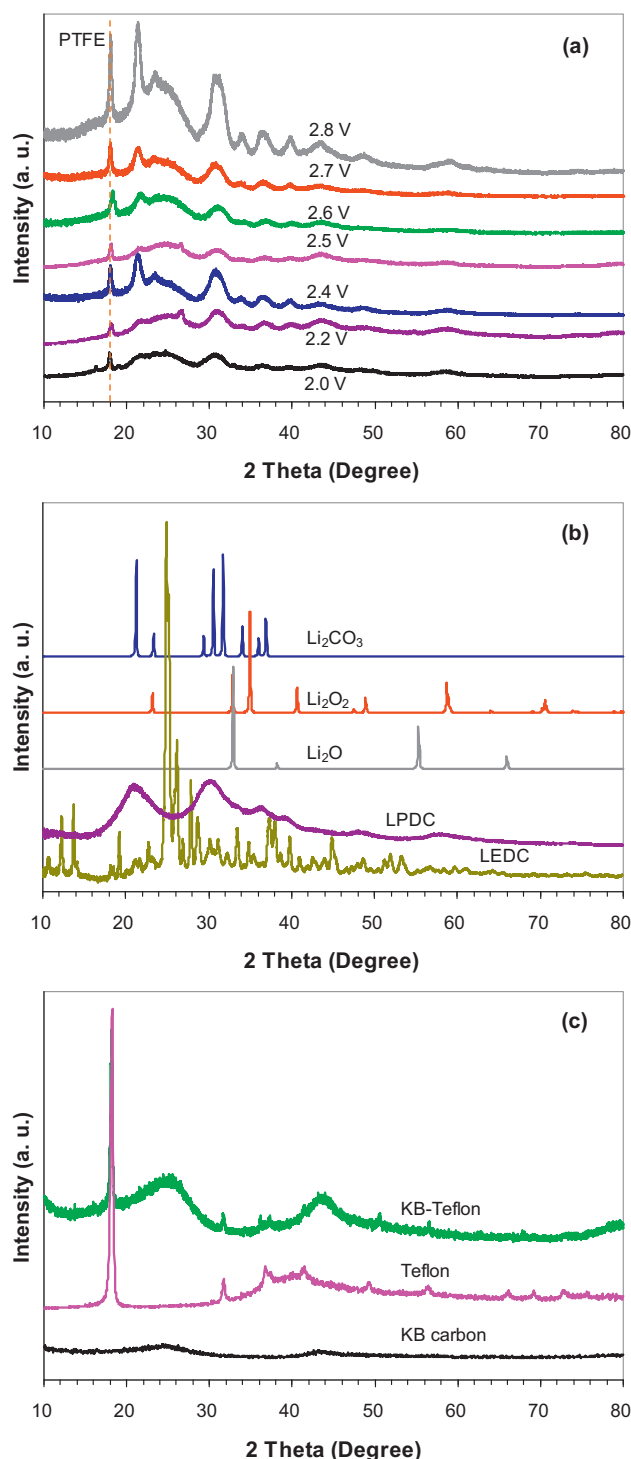


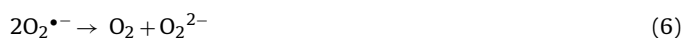
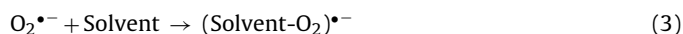
Fig. 2. XRD patterns of the air electrodes discharged at different DOD (a), with comparisons of the standard chemicals of (b) Li₂CO₃, Li₂O₂, Li₂O, LEDC and LPDC, and (c) KB carbon, Teflon and KB-Teflon air electrode.

tion product of PC seem to prevail with the characteristic broad peaks, which are likely attributed to the less crystalline nature arising from the methyl group. At 2.0 V DOD some new peaks appear, demonstrating the appearance of newly formed crystalline phase for LEDC and/or other compounds.

At the onset of Li–O₂ chemistry, it is believed that an oxygen molecule is reduced to form a superoxide radical anion (O₂^{•-}) after extracting one electron from carbon air electrode [19,20].



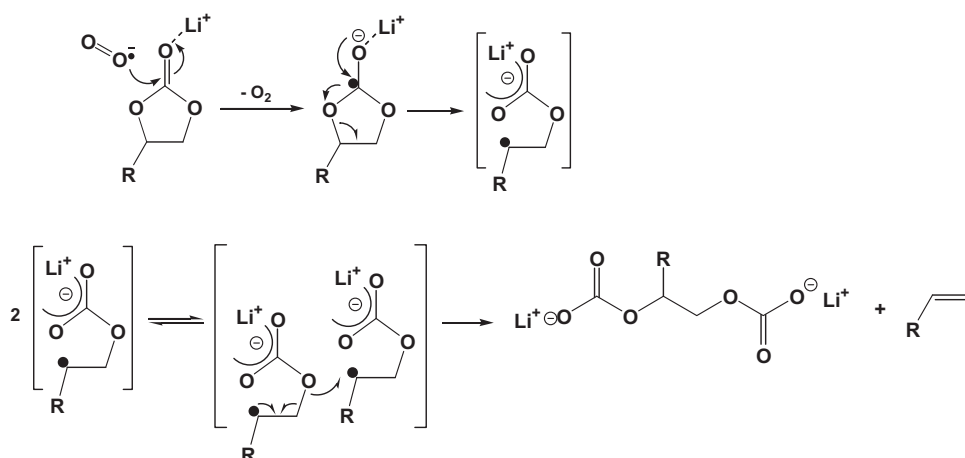
The superoxide radical anion is instantaneously solvated by the solvent molecules around it. The single-electron reduction potential of O_2 , $E^\circ(O_2/O_2^{\bullet-})$, which is one of the most important characteristics of superoxide radical anion, is widely accepted to be -0.33 V (1 atm O_2) vs. normal hydrogen electrode (NHE) in aqueous solutions and -0.45 to -0.75 V vs. NHE in different aprotic solvents [19]. The resultant superoxide radical anion can coordinate with one Li^+ ion to form an intermediate product – lithium superoxide (LiO_2) (reaction (2)) and precipitate on the air cathode [2,19,20], and/or attack a solvent molecule by the nucleophilic mechanism (reaction (3) below). Reactions (2) and (3) are competitive depending on the stability of the solvent molecules in the vicinity of the superoxide radical anion. LiO_2 is not thermodynamically stable and would transiently convert to Li_2O_2 through either a chemical (reaction (4)) and/or an electrochemical pathway (reaction (5)), as proposed by Abraham and co-workers [13]. Alternately, Aurbach et al. [20] suggested that Li_2O_2 was formed by the reaction of a Li^+ ion and a peroxide anion (O_2^{2-}) (reaction (8)) that was formed through the disproportionation (reaction (6)) and/or electrochemical reaction of superoxide radical anions (reaction (7)).



Regardless of the formation mechanism, if the solvent in the electrolyte is chemically stable with the superoxide radical anion, the chemical reaction depicted in reaction (3) would hardly proceed. Then reactions (2) and (4)–(8) become dominant, with Li_2O_2 becoming the main product in the air electrode. However, if the solvent in the electrolyte is chemically reactive toward the superoxide radical anion, the solvent molecules can then be reduced and form new radicals and/or anions, leading to species originating from the solvents. While the relative rates of the reactions identified above are not known, the XRD results of the discharged air electrodes in organic-carbonate-based electrolytes imply that the attack of the solvent molecule by superoxide radical anion (reaction (3)) happens at faster rate than does the coordination of the superoxide radical anion with the Li^+ ion to form LiO_2 (reaction (2)).

If the formation of LiO_2 does occur first, despite the fact that LiO_2 is a strong Lewis base and can react with the carbonate solvents to form lithium alkylcarbonates and Li_2CO_3 (because PC and EC are good substrates for the nucleophilic attack as reported previously by Aurbach et al. [20,21]), at least some of the LiO_2 will still lead to the formation of Li_2O_2 via the disproportionation reaction (reaction (4)) and electrochemical reaction (reaction (5)). Previously we have found that the reaction between Li_2O_2 and carbonate solvents only occurs with long exposure (24 h) to high temperature ($\sim 150^\circ\text{C}$) in order for some lithium alkylcarbonates and/or Li_2CO_3 to form (Fig. 3). On the other hand, Li_2O_2 and PC in contact at room temperature for one week shows nearly no change to the XRD pattern of Li_2O_2 (Fig. 3). Thus, we firmly believe that the kinetic rate of the reaction between Li_2O_2 and carbonate molecules is so slow under the normal cycling conditions that its possibility is negligible. In other words, both EC and PC should be sufficiently stable with Li_2O_2 , which in turn should be detected by XRD due to this stability. However, because essentially no Li_2O_2 has been detected, the spectra in Fig. 1 actually serves as a rather strong implication that the formed superoxide radical anions have been preferably and rapidly consumed by the nucleophilic attack on the carbonate solvents (reaction (3)), leading to the formation of new radicals and alkylcarbonate anions via ring-opening of either EC or PC. A possible mechanism, which is similar to related reductive processes of these same organic carbonate molecules in the Li-ion battery environment, is proposed in Scheme 1.

The newly formed radicals may initiate further ring-opening reactions of the solvent molecules to form long-chain oligomers or even polymers, while the latter alkylcarbonate anions may coordinate Li^+ ions to form lithium alkylcarbonates (such as LPDC, LEDC, and others in this case) and precipitate onto the air cathode, which in turn may further decompose or react with moisture or other acidic impurities in the electrolyte and air electrode, eventually leading to Li_2CO_3 and other compounds. This interpretation is in excellent agreement with the spectroscopic observation of lithium alkylcarbonates and Li_2CO_3 and the absence of Li_2O_2 and Li_2O . It also agrees with the finding that very similar species form from carbonate electrolytes regardless of the DOD. Thus, it could be tentatively concluded that the discharging process of a Li–O₂ chemistry in carbonate-based electrolytes actually consists of initial single-electron reduction of O_2 into superoxide radical anion ($O_2^{\bullet-}$) and the subsequent nucleophilic attack by it onto the organic carbonate solvents, forming the eventual lithium alkylcarbonates that have been well known on anode surfaces of Li-ion batteries.



Scheme 1. A possible reduction mechanism of cyclic carbonate solvents by the attack of a superoxide radical anion, where $R=H$ or CH_3 in this work.

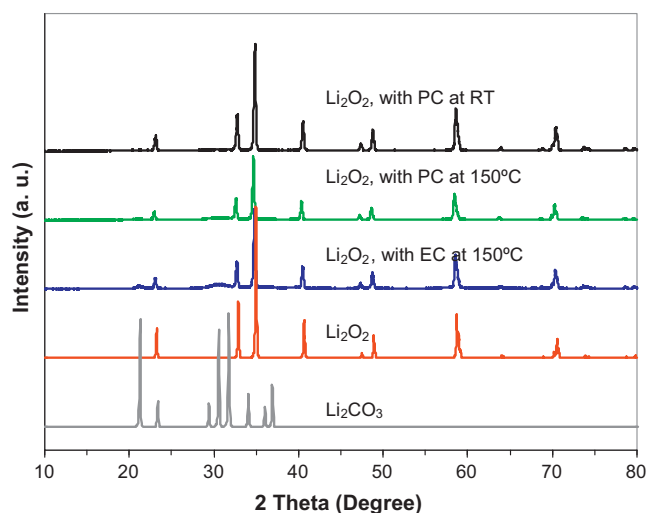


Fig. 3. XRD patterns of Li_2O_2 powders after mixing with PC and EC at 150 °C for one day and with PC at room temperature for one week, with comparisons of the standard chemicals of Li_2CO_3 and Li_2O_2 .

3.2. Re-oxidative processes upon charging

It has been reported in literature that Li– O_2 batteries with carbonate-based electrolytes can be recharged up to 100 cycles depending on the catalysts and electrolytes used [7–12]. The previously accepted rationale of this reversibility was based on the assumption that these Li– O_2 systems had desirable redox reactions at the air electrodes within the voltage windows such systems operate; that is, O_2 received electrons during the discharging process at $\sim 3.0\text{V}$ and was reduced to peroxide or oxide anions, which, after coordinating with Li^+ cations, formed lithium peroxide or lithium oxide (reactions (9) and (10)), and these reactions were reversed via re-oxidization of peroxide or oxide salts at $>4.0\text{V}$ during the charging process to release O_2 and Li^+ ions (reactions (11) and (12)).



This rationale has recently been challenged by the newly established fact that lithium alkylcarbonates and Li_2CO_3 , rather than Li_2O_2 or Li_2O , are the main discharge products when carbonate-based electrolytes are used [12,14,15]. Then we face a new question: are these lithium alkylcarbonates and/or Li_2CO_3 reoxidizable? Fig. 4 shows the cyclability of the air electrodes pre-loaded with different starting active materials, including SP, Li_2CO_3 , LEDC, LPDC, Li_2O_2 , and Li_2O , in an O_2 atmosphere (ca. 1 atm) at room temperature. All the air electrodes were first charged from open circuit potentials to 4.5 V and then cycled between 2.0 and 4.5 V, where the current was set 30mA g^{-1} of the total amount of SP and active material. It is seen that poor cycle life is observed for all the SP air electrodes with preloaded lithium oxides or salts.

The first cycle charge capacities of SP and Li_2CO_3 electrodes are 4.1mAh g^{-1} and 4.8mAh g^{-1} , respectively, when charged to 4.5 V and based on the weight of the same individual material. It has been found that nearly the same capacities are obtained for the two electrodes when charged to 4.6 V (data not shown here). This indicates that both chemicals are electrochemically inert and cannot be oxidized. This small charge capacity ($<5\text{mAh g}^{-1}$) arises mainly from the decomposition of electrolyte components, and is expected to increase with the use of a high-surface-area carbon material in the

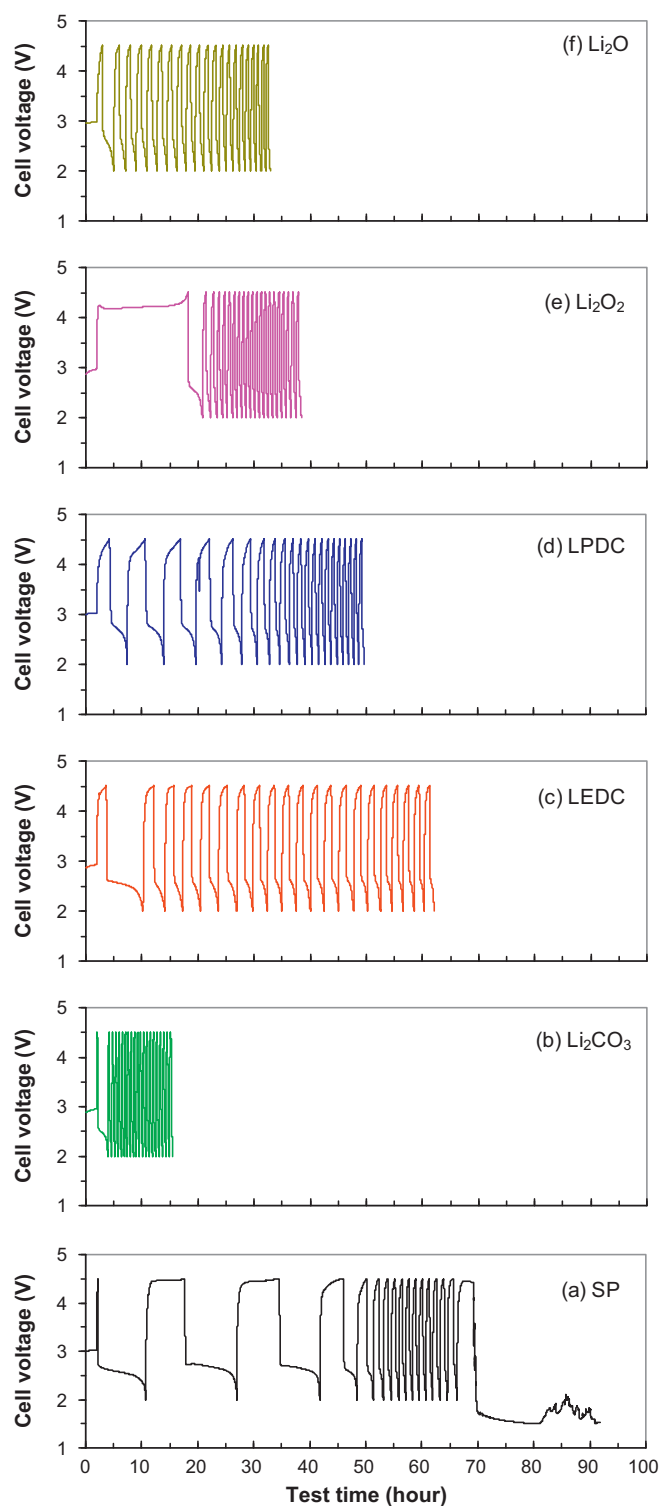


Fig. 4. Cyclability of different air electrodes between 4.5 V and 2.0 V at 30mA g^{-1} of the weight of SP and active material. (a) SP/PVDF (8:2 by wt), (b) Li_2CO_3 /SP/PVDF (4:4:2 by wt), (c) LEDC/SP/PVDF (4:4:2 by wt), (d) LPDC/SP/PVDF (4:4:2 by wt), (e) Li_2O_2 /SP/PVDF (4:4:2 by wt), and (f) Li_2O /SP/PVDF (4:4:2 by wt).

air electrode as it is known from the studies of Li-ion batteries that the electrolyte decomposition is largely related to the surface area of the electrode materials.

The charge capacities of LEDC and LPDC during the first charging process are, on the other hand, 99.6mAh g^{-1} and 153.3mAh g^{-1} , respectively, while the corresponding theoretical specific capaci-

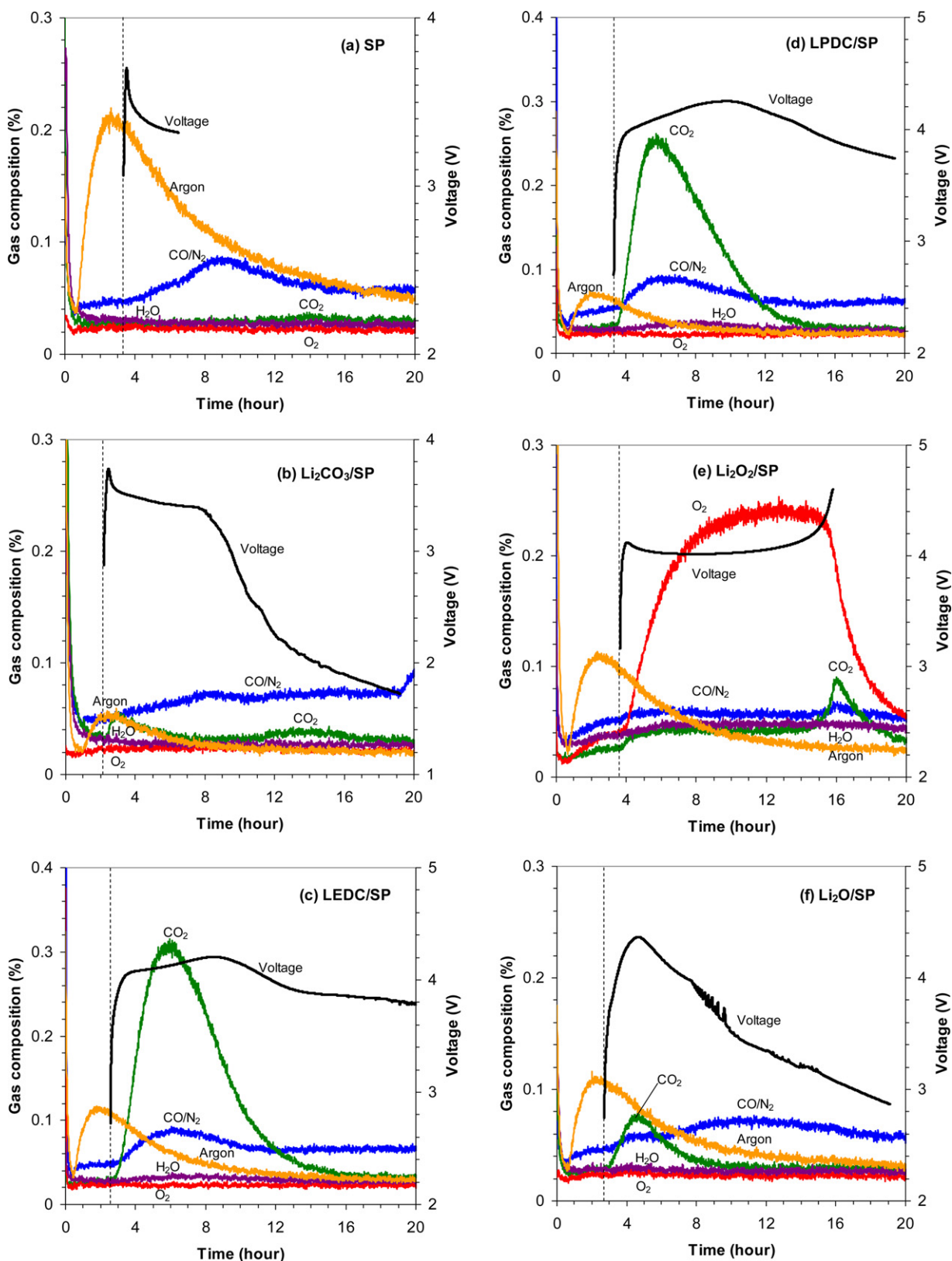


Fig. 5. Variations of gas compositions for different air electrodes during the charging process. (a) SP/Fe₃O₄/PVDF, (b) Li₂CO₃/SP/Fe₃O₄/PVDF, (c) LEDC/SP/Fe₃O₄/PVDF, (d) LPDC/SP/Fe₃O₄/PVDF, (e) Li₂O₂/SP/Fe₃O₄/PVDF and (f) Li₂O/SP/Fe₃O₄/PVDF in the electrolyte of 1.0M LiTFSI in PC-EC (1:1 by wt), where a vertical dotted line is plotted to indicate the start of the charging process.

ties are 237.2 mAh g⁻¹ for LEDC and 223.3 mAh g⁻¹ for LPDC based on two-electron reactions. Because the capacity contribution from the electrolyte decomposition on the conductive carbon SP is negligible, the efficiency of LEDC and LPDC being oxidized during the first cycle is 42.0% and 68.7%, respectively. Therefore both LEDC and LPDC can be considered as oxidizable active species although the charging efficiency remains moderate.

In comparison, when the Li₂O₂ electrode is charged to 4.5 V, the first charge capacity is 970.7 mAh g⁻¹. Considering that the purity of Li₂O₂ used is only 90%, the charge capacity based on pure Li₂O₂ is about 1078.6 mAh g⁻¹. The theoretical specific capacity of Li₂O₂ is known to be 1168 mAh g⁻¹; thus, a 92.3% utilization of Li₂O₂ during the first charging process is obtained, which is very close to our previously reported result [15].

Meanwhile, a charge capacity of 63.3 mAh g⁻¹ can be extracted from Li₂O electrode, seemingly indicating its partial rechargeability. However, as indicated by the GC/MS test results (Fig. 5(f)) that will be discussed in more detail below, charging the Li₂O electrode does not generate O₂, but CO₂ and CO instead, involving a new mechanism other than reaction (12).

Fig. 5 shows the variations of gas compositions during the first charging process for the six air electrodes: (a) SP/Fe₃O₄/PVDF, (b) Li₂CO₃/SP/Fe₃O₄/PVDF, (c) LEDC/SP/Fe₃O₄/PVDF, (d) LPDC/SP/Fe₃O₄/PVDF, (e) Li₂O₂/SP/Fe₃O₄/PVDF and (f) Li₂O/SP/Fe₃O₄/PVDF in the electrolyte of 1.0 M LiTFSI in PC–EC (1:1 by wt). In the figures, the vertical dotted line indicates the start of the charging process. The charging was conducted in a helium atmosphere with continuous helium gas flow through the Teflon container, and the cutoff voltage was set at 4.6 V. Only the signals of Ar, CO₂, CO/N₂, O₂, and H₂O are selected to make the plots for comparison. Because CO and N₂ are isobaric species (m/e=28), no effort was made to differentiate these two components, but

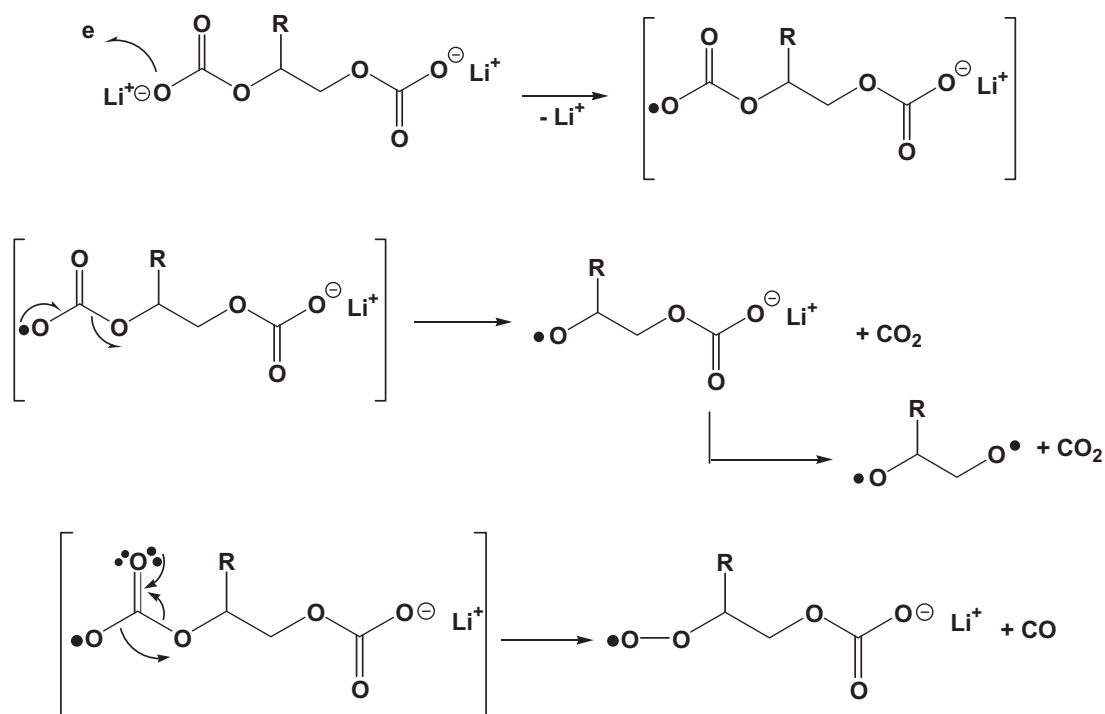
the qualitative analysis based on the trend of CO concentration changes during the charging process should not be affected.

We found from the tests that, with the exception of the Li₂O₂ electrode, none of the other five electrodes can reach the pre-set cutoff voltage (4.6 V) during the charging process. The cell voltage decreases after reaching a maximum and may drop rapidly during the following charging process. Two to three cells for each kind of electrode were tested under the same conditions and all cells showed reproducible trends during the charging process in a helium atmosphere. This phenomenon also was reported previously for the Li₂O₂ electrode during the second charging process [15]. However, as shown in Fig. 4, the voltage decrease during charging process does not happen to any of these electrodes when cycled in an O₂ atmosphere. It is apparent that the ambient gas has effect on the charging process of the air electrodes. One possible explanation is as below: Ni substrate has been continuously oxidized to Ni²⁺ in inert atmosphere, which causes the anodic dissolution of Ni metal [22] thus the cell voltage is unable to be charged up; while in O₂ atmosphere, the Ni metal on the surface of the Ni substrate has been oxidized to NiO during charging that well passivate the Ni substrate so that no further loss of Ni would occur and then the cell can be charged normally. However, the underlying reason needs to be further investigated.

It is seen from Fig. 5(a) that, after the charging process started, the SP electrode mainly released increasing amount of CO. Charging was stopped after 3 h, but CO was continually generated. While trace amount of CO₂ was also detected after 10 h of charging, no H₂O and O₂ were formed. The CO generation can be attributed to the decomposition of the electrolyte at the high-surface-area activated carbon.

The Li₂CO₃ electrode generated a small amount of CO₂, accompanied by a continuous increase in the amount of CO generated

electron extracted by electrode



Scheme 2. A possible oxidation mechanism of lithium alkylcarbonates, where R = H or CH₃ in this work.

during the 17-h charging process (Fig. 5(b)). Similar to SP electrode, no H₂O and O₂ were detected. During the electrode preparation processes, minor to medium gellation of the slurries was observed for the Li₂CO₃ and Li₂O₂ electrodes, and significant gellation was noticed for the LEDC, LPDC and Li₂O electrodes. No gellation was found for the SP electrode. Gellation is believed to be caused by the attack of the PVDF binder and NMP solvent by these chemicals, with the possible formation of polymers with higher molecular weights. These new materials are probably decomposed during charging and release CO₂ and CO, which is the primary reason for the evolution of small amounts of CO₂ and CO from the charging to the Li₂CO₃, Li₂O₂, and Li₂O electrodes.

Compared to all the other standard references investigated in this work, the electrodes pre-loaded with LEDC and LPDC showed rapid releases of CO₂ in large amount when the charging process started (Fig. 5(c) and (d)). The amount of CO₂ released was greater than the amount expected from the decomposition of the gelled PVDF–NMP materials as discussed above. Some CO and minor H₂O also were formed, but no O₂ was generated. This indicates that these lithium alkylcarbonates are oxidizable, but this oxidation process is irreversible because of the significant loss of carbon species in the form of CO₂ and CO.

In Scheme 2, we propose a possible general mechanism for the oxidation of these alkylcarbonates on the surface of the air cathode. A more thorough investigation will need to be undertaken to define the exact chemistry. These oxide or peroxide radicals should be sufficiently stable for electron-spin resonance analysis, and their fate, with possibilities of further reacting with organic carbonate molecules, remains unclear at this moment.

It is self-evident from the mechanism shown in Scheme 2 that the reversibility of such a Li–O₂ chemistry is non-sustainable on multiple levels. Even if these alkylcarbonates can be readily re-oxidized upon charging (which is not really true considering the conversion efficiency evaluated above), the entire process is still based on the consumption of the organic carbonate solvent, which is a limited source in a Li–O₂ battery.

As reported previously [15], the Li₂O₂ electrode can be charged to release O₂ in high yield and with good efficiency (Fig. 5(e)). The small amount of CO₂, CO and H₂O observed is mainly from the decompositions of the gelled PVDF–NMP materials and the electrolyte as discussed above.

When charging the Li₂O electrode (Fig. 5(f)), no O₂ was found but only certain amounts of CO₂ and CO were detected, thus indicating that Li₂O cannot be re-oxidized.

The six air electrodes without Fe₃O₄ catalyst—SP/PVDF (8:2 by wt), Li₂CO₃/SP/PVDF (4:4:2 by wt), LEDC/SP/PVDF (4:4:2 by wt), LPDC/SP/PVDF (4:4:2 by wt), Li₂O₂/SP/PVDF (4:4:2 by wt), and Li₂O/SP/PVDF (4:4:2 by wt)—all showed similar gas formation during charging in an inert gas atmosphere, but slightly less CO₂ and CO were generated.

In summary, from the results presented and discussed in this paper, it is known that the main discharge products on the carbon air electrodes from carbonate-based liquid electrolytes are lithium alkylcarbonates and Li₂CO₃, among which the two alkylcarbonates LEDC and LPDC are oxidizable but Li₂CO₃ is not up to 4.6V. The alkylcarbonates release CO₂ and CO upon oxidation, but further studies need to be undertaken to determine the exact chemistry. We believe that the cycling of all the six electrodes in the PC–EC-based electrolyte, as shown in Fig. 4, is actually based on decompositions of (1) carbonate solvents during discharging and (2) lithium alkylcarbonates during charging. Because of the covering of the carbon–air electrode surface and blocking of the porous structure by the electrolyte decomposition products during the discharging process and the poor charging efficiency of lithium alkylcarbonates, the capacity and the coulombic efficiency of a Li–O₂ or Li–air battery with a carbonate-based electrolyte will

decrease at steady rates with the cycling numbers, thus resulting in poor cell performance and a short cycle life.

4. Conclusions

A systematic investigation was conducted on the cyclability of Li–O₂ chemistry in liquid organic carbonate electrolytes. XRD results indicate that the majority of the discharge products from carbonate-based electrolytes are lithium alkylcarbonates and Li₂CO₃, regardless of the DOD, while nearly no Li₂O₂ and Li₂O are formed. The DOD has a little effect on the crystallinity of the discharged products. By lowering the DOD from 2.8 V down to 2.2 V a decrease of crystallinity is observed. Results from an *in situ* GC/MS test indicates that Li₂CO₃ and Li₂O cannot be oxidized up to 4.6 V. Li₂O₂ is able to be oxidized to form O₂ at high efficiency, but lithium alkylcarbonates (e.g. LEDC and LPDC) are oxidizable to release mainly CO₂ and CO. Cycling of Li–O₂ batteries in organic carbonate electrolytes is thus based on the sequence of reductively forming of alkylcarbonate from the electrolyte solvent during discharging and oxidative decomposition of these same alkylcarbonates upon charging. Therefore, this chemistry is not sustainable to support a reversible Li–O₂ chemistry. The most important challenge that must be overcome for rechargeable Li–O₂ batteries is to identify new electrolyte systems that can ensure the exclusive formation of Li₂O₂ on air electrodes. In other words, non-aqueous electrolyte solvents that can remain chemically stable against superoxide radical anions while maintain electrochemical stability during charging process must be identified.

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