Short communication

Kinetic investigation of catalytic disproportionation of superoxide ions in the non-aqueous electrolyte used in Li–air batteries

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HIGHLIGHTS

- Superoxide formed during the reduction of O_2 can react with PC.
- The superoxide ions can also become disproportionated catalyzed by Lewis acid.
- The catalytic disproportionation for $O_2^{\bullet-}$ is much faster than its reaction with PC.
- The chemical reaction between PC and $O_2^{\bullet-}$ can be minimized.

ABSTRACT

Superoxide reacts with carbonate solvents in Li–air batteries. Tris(pentafluorophenyl)borane is found to catalyze a more rapid superoxide (O_2^-) disproportionation reaction than the reaction between superoxide and propylene carbonate (PC). With this catalysis, the negative impact of the reaction between the electrolyte and O_2^- produced by the O_2 reduction can be minimized. A simple kinetic study using ESR spectroscopy was reported to determine reaction orders and rate constants for the reaction between PC and superoxide, and the disproportionation of superoxide catalyzed by Tris(pentafluorophenyl)borane and Li ions. The reactions are found to be first order and the rate constants are 0.033 s^{-1} M^{-1}, 0.020 s^{-1} M^{-1} and 0.67 s^{-1} M^{-1} for reactions with PC, Li ion and Tris(pentafluorophenyl)borane, respectively.

1. Introduction

Li–O_2 battery chemistry has aroused significant interests due to its high theoretical specific capacity, which far exceeds state-of-art Li-ion batteries, due to the cathode active material (O_2) being abundant in the air. However, before Li–air chemistry becomes applicable, there are many technical obstacles that need to be addressed. Among them is the chemical reaction between the superoxide ($O_2^{\bullet-}$) and many carbonate solvents e.g. propylene carbonate (PC). $O_2^{\bullet-}$ has been identified as the product of 1-e O_2 reduction in non-aqueous electrolytes [1–3]. $O_2^{\bullet-}$ can react with organic solvents and specially carbonate solvents. The reaction will not only consume the electrolyte but also form undesired non-rechargeable products e.g. Li_2CO_3 [4,5]. Efforts have been made to search for the solvents which resist to react with $O_2^{\bullet-}$ [6,7]. We believe that the chemical interaction between the superoxide ions

and the electrolyte is one of a few competing parallel reactions that $O_2^{\bullet-}$ may undergo, the disproportionation $O_2^{\bullet-}$ would be another possible reaction. To alleviate the problems associated with the $O_2^{\bullet-}$/ electrolyte reactions, we have attempted to facilitate the rapid disproportionation, while hindering its chemical interaction with the electrolyte. Peroxide ions (O_2^{2-}) act as a Lewis base and can be stabilized by strong Lewis acid. When a strong Lewis acid–base complex is formed, $O_2^{\bullet-}$ could be driven to disproportionate to O_2 and encapsulated O_2^{2-}. Tris(pentafluorophenyl) borane (TPFPB) is a strong boron-based Lewis acid. Indeed, we discovered that TPFPB can catalyze rapid disproportionation of $O_2^{\bullet-}$. Such catalytic disproportionation of $O_2^{\bullet-}$ is much faster than its chemical reaction with aprotic electrolyte [8], so the $O_2^{\bullet-}$ ions become disproportionated before reacting with the solvents. Therefore the issues associated with the chemical interaction between $O_2^{\bullet-}$ and the electrolyte can be alleviated. In this paper, we reported the quantitative determination of the reaction rate constants for the catalytic disproportionation.

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2. Experimental details

All reagents were purchased from Sigma−Aldrich except tris(-pentafluorophenyl) borane (TPFPB) which was synthesized in-house at Brookhaven National Laboratory according to the procedures reported in the literature [9]. Anhydrous grade propylene carbonate (PC) and dimethyl sulfoxide (DMSO) were further dried in-house using 5 Å molecule sieves, which were vacuum dried at 400 °C before use. The moisture in PC and DMSO was less than 20 ppm as measured by Karl Fisher titration. The purity of 1.1-diphenyl-2-picrylhydrazyl (DPPH) was determined by UV visible spectroscopy as its absorptivity at 520 nm in ethanol is 12350 lM^{-1} cm^{-1} [10,11]. The purity was found to be 93.8%.

Electron Spin Resonance (ESR) measurements were conducted using an ESR spectrometer model CMS8400 made by Resonance Instrument, Inc.

A standard for a quantitative ESR measurement is a stable material with a known number of spins that has similar line shape and width. Pure paramagnetic compounds with known spin concentrations are normally used as primary standards. MnO_2 diluted in MgO ($S = 5/2$) and DPPH (free radical, $S = 1/2$) were proven as reliable primary standard for quantitative ESR spectroscopy [11]. DPPH was chosen in our experiments as ESR standard. DPPH is the oldest and most commonly used ESR standard. Its g-value is 2.0037 ± 0.0002 and is independent from the solvent. DPPH also has the same spin quantum number as O_2^{-}. Five samples with gradually increased concentrations were prepared by dissolving the carefully weighed DPPH in DMSO solvent. 280 µl of the standard solutions were transferred into ESR sample tubes (outer diameter 4 mm). The sample tube was then placed carefully into the cavity of ESR instrument so that it was vertically and horizontally centered in the cavity, which is critical for accurate measurements [12–14].

The kinetic experiments were conducted by injecting the catalysts (TPFPB and Li salt) or reactant (PC) into KO_2 DMSO solution. The decrease of O_2^{-} concentration was monitored by ESR at −50 °C. Catalytic disproportionation of O_2^{-} is a very fast reaction [8]. In order to acquire an adequate amount of data points, low O_2^{-} concentration and a small amount of TPFPB were used. 0.15 M 18-crown-6 DMSO solution was used to assist the dissolution of KO_2. During the kinetic experiments, a small amount of reactant or catalyst was injected in 280 µl of 0.0108 M of KO_2 DMSO solution. After certain duration at 22 °C, the sample tube was put in the ESR cavity kept at −50 °C, at which temperature ESR measurements were taken. At −50 °C, both the chemical reaction and disproportionation ceased, while the intensity of O_2^{-} signal remained constant at the temperature. The sample tube was then taken out of the cavity and warmed up to 22 °C in a water bath allowing the reaction to proceed periodically. It took about 15 s to warm up the sample to 22 °C.

3. Results and discussion

Electron Spin Resonance (ESR), also known as electron paramagnetic resonance (EPR), is a unique technique for the investigation of species containing unpaired electrons like the superoxide ion, O_2^{-}. The concentration of the species can be determined by measuring the spin concentration, since the spin number is proportional to the amount of species. One of the most difficult tasks in ESR is the quantitative ESR measurement of the spin number. The most practical and reliable way to determine the spin concentration is to compare the integrated area of the sample spectrum with that of an appropriate standard, as the method of absolute spin concentration estimation is difficult and even impossible in some cases. In the current investigation, DPPH was used as standard since
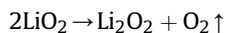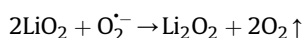
both O_2^{-} and DPPH are free radicals, S is ½. It has been reported that DPPH will remain stable in the solution at room temperature with its ESR signal unchanged for many days [12]. The spin concentration of the superoxide and the standard was determined from the double integration of the ESR peak. Assuming the Curie law was followed, the ratio of the number of spins or spin concentration (spin/cm) of O_2^{-} and DPPH can be expressed as [12]:

$$\frac{N_{O_2^{-}}}{N_{DPPH}} = \frac{g_{O_2^{-}}}{g_{DPPH}} \frac{S_{O_2^{-}}\left(S_{O_2^{-}} + 1\right)A_{O_2^{-}}}{S_{DPPH}(S_{DPPH} + 1)A_{DPPH}}$$

where A is the double integrated area, g is the average g value and S ($S = 1/2$ for both O_2^{-} and DPPH) is the spin. The average g values for the O_2^{-} and DPPH are both around 2.0023.

A standardization curve was first generated using DPPH DMSO solutions with known concentration. The standardization curve is shown in Fig. 1. A clear linear relationship is demonstrated for quantitative analysis. Therefore, the concentration of O_2^{-} can be determined from the double integration of the ESR peak.

Non-catalyzed disproportionation of O_2^{-} has greater enthalpies than the difference between singlet state and triplet state of O_2; therefore, O_2^{-} is relatively stable in aprotic solvents e.g. DMSO. The stability of O_2^{-} in DMSO solution was demonstrated in our previous publication [8], where there were no apparent changes of O_2^{-} ion after 12 h storage at room temperature. However, if there exists a Lewis acid, even as Li^+, the disproportionation of O_2^{-} becomes thermodynamically favorable [14]

$$O_2^{\bullet-} + Li^+ \rightarrow LiO_2$$

$$2LiO_2 + O_2^{\bullet-} \rightarrow Li_2O_2 + 2O_2 \uparrow$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \uparrow$$

In a Li−air battery, Li salts are normally used in the electrolyte; therefore the catalytic disproportionation by Li ion was of interest to be investigated. Fig. 2 shows the ESR spectra taken at the different times for the solution of 0.01 M KO_2 DMSO with 0.2 M of $LiBF_4$ added. It is clearly evident that O_2^{-} was consumed by the disproportionation catalyzed by Li ions in the electrolyte.

O_2^{-} ion is a powerful nucleophile in aprotic solvents. In particular, it subjects PC to a ring-opening attack that produces a variety
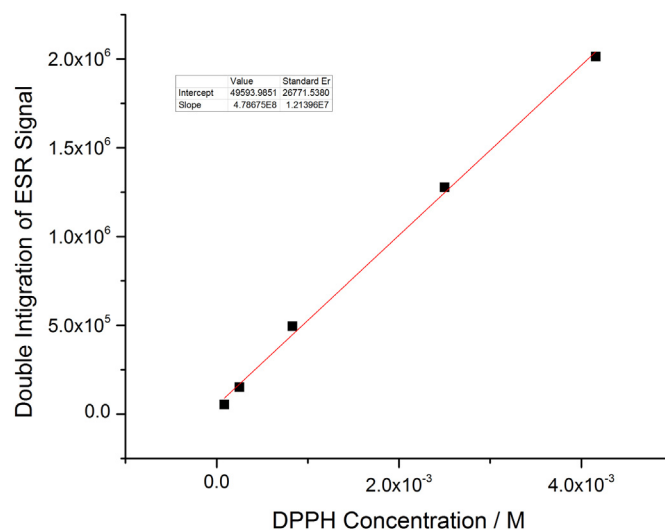

Fig. 1. Calibration curve of DPPH.