



# Oxygen Redox Reaction in Lithium-based Electrolytes: from Salt-in-Solvent to Solvent-in-Salt



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## ABSTRACT

Electrolytes are key components of Li/O<sub>2</sub> batteries. The ionic liquid-like structure and good electrochemical and thermal stability of solvent-in-salt electrolytes make them of great interest for lithium batteries. Solutions of lithium bis(trifluoromethanesulfonyl)imide in tetraethylene glycol dimethyl-ether with molar ratios ranging from 1:9 to 1:0.9 are here investigated. A voltammetric study of oxygen redox reaction in presence of different concentrations of salt, from salt-in-solvent to solvent-in-salt solutions, is reported here for the first time along with a novel luminescence method for the evaluation of O<sub>2</sub> solubility. The results indicate that superconcentrated solutions favor the solution formation mechanism of Li<sub>2</sub>O<sub>2</sub> during discharge which in turn is beneficial for battery cycling stability. Despite the higher viscosity of solvent-in-salt solutions than conventional electrolytes, O<sub>2</sub> solubility is improved at the highest salt concentrations. These findings contribute to understand electrochemical processes in solvent-in-salt solutions for Li/O<sub>2</sub> and next generation metal-based batteries.

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## 1. Introduction

In recent years, the very high theoretical specific energy of Li/O<sub>2</sub> batteries, comparable to gasoline value, has attracted the interest of researchers [1]. The oxygen redox reaction (ORR) in non-aqueous electrolytes involves the formation of lithium superoxide (LiO<sub>2</sub>) that evolves to lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) via chemical disproportionation and electrochemical processes [2]. Discharge products and mainly superoxide are highly reactive species that cause electrolyte and carbon cathode degradation [3–5]. Insoluble Li<sub>2</sub>O<sub>2</sub> clogs the cathode surface during battery discharge and brings about high recharge overpotentials. Battery cycling stability is, therefore, affected by electrolyte chemical and electrochemical stability and by the electrode passivation with solid Li<sub>2</sub>O<sub>2</sub> [6,7]. Electrolytes in Li/O<sub>2</sub> batteries have to be resistant towards the superoxide (O<sub>2</sub><sup>•−</sup>) and peroxide (O<sub>2</sub><sup>2−</sup>) ions formed during discharge, should feature good oxidative resistance, high O<sub>2</sub> solubility and mass transport, and should be engineered in order to promote the Li<sub>2</sub>O<sub>2</sub> solution formation mechanism vs. the surface

growth [6,8–11]. Indeed, the formation in solution of Li<sub>2</sub>O<sub>2</sub> particles that, then, agglomerate on the electrode as large clusters keeps part of the carbon surface free from passivation. This enables high discharge capacities. Instead, surface growth mechanism produces highly passivating thin film on electrode surface that accelerates cell death [3,6,12]. The two mechanisms are driven by the stability of the superoxide anion in solution, which in turn depends on solvent donor number (DN) and on electrolyte cation Lewis acidity [13,14]. High-DN solvents and soft Lewis acid cations promote the solution mechanism and stabilize the superoxide (soft Lewis base). Low-DN solvents and hard Lewis acid cations, like free Li<sup>+</sup> ions, facilitate the surface mechanism and superoxide disproportionation to peroxide (hard Lewis base) [6,12,15]. Solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl-ether (TEGDME) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI) ionic liquid (IL) are known for their wide electrochemical stability window, high chemical oxidation stability, high compatibility with Li metal, high Li<sup>+</sup> ion transport rate and good oxygen transport properties, which are key features for a Li/O<sub>2</sub> battery [16,17]. TEGDME is of particular interest for its low dielectric constant that favors oxygen solubility [18]. Table 1S compares dielectric constant, viscosity, O<sub>2</sub> solubility and DN of solvents commonly used in lithium battery electrolyte formulations. Recently, "solvent-in-salt" (SIS) solutions, featuring salt-to-

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solvent ratio in weight or volume greater than 1, have been proposed as key electrolytes for lithium batteries, including Li/S and Li/O<sub>2</sub> batteries [19–23]. Mandai et al. proposed SIS electrolytes based on LiTFSI in TEGDME and demonstrated that when the salt-to-solvent molar ratio approaches 1:1 the solutions have an IL-like structure with independent [Li(glyme)]<sup>+</sup> cation complexes and TFSI<sup>-</sup> anions, as shown in the right side of Fig. 1 [24].

Li et al. explored solutions with different LiTFSI-to-TEGDME molar ratios in the range 1:7 to 1:1 in Li/O<sub>2</sub> cells [21]. The best capacity retention and discharge voltage stability was achieved at the 1:5 ratio, out of the SIS range. This ratio was considered the best compromise to alleviate the reactivity of O<sub>2</sub><sup>•-</sup> with both the free glyme (at lower molar ratios) and the glyme of the [Li<sup>+</sup>(glyme)<sub>1</sub>⋯O<sub>2</sub><sup>•-</sup>] complex (at higher molar ratios). The study mainly relied on galvanostatic charge/discharge performance of 2-electrode Li/O<sub>2</sub> cells, where both cathode and anode processes play a role. Lithium is expected to affect cell performance, too, and solid electrolyte interface (SEI) stability at the lithium metal anode has been demonstrated to improve by the use of SISs [22,23]. However, the work by Li et al. did not include a specific electrochemical study of cathode ORR reactions [21].

There is no general acceptance on the mechanism of ORR in a wide range of salt concentrations in aprotic solvents. This work addresses this issue by a voltammetric study in LiTFSI-TEGDME solutions in both the salt-in-solvent and SIS regions. The study is supported by a novel luminescence method for the evaluation of O<sub>2</sub> solubility.

## 2. Experimental

### 2.1. Materials and chemical-physical characterization of the solutions

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, ≥99%, Aldrich) and tetraethylene glycol dimethyl ether (TEGDME, 99%, Aldrich, 20 ppm of H<sub>2</sub>O) were both used as received. The LiTFSI-TEGDME solutions were prepared and stored in dry box (MBraun, O<sub>2</sub> and H<sub>2</sub>O < 1 ppm). The physical chemical characterization comprises density and viscosity measurements, ionic conductivity

tests and thermogravimetric analyses. The density was calculated after weighting three volumetric flasks with 5 mL of each solution (class A glassware, uncertainty ± 0.025 mL) at a temperature of 22 °C ± 1 °C and atmospheric pressure (0.1 ± 0.01 MPa). Viscosity was measured using a ViscoClock unit combined with a Micro-Ubbelohde viscometer (SI Analytics) at 22 °C ± 1 °C and atmospheric pressure (0.1 ± 0.01 MPa). A capillary with a diameter of 0.53 mm was used for solutions from 0 to 2 m, instead a larger capillary (Ø 0.96 mm) was used from 3 m to 5 m solutions. The accuracy on the flow time is 0.01% with 95% confidence level. Ionic conductivity was investigated in the range -20 °C/80 °C. It was measured by CDM 210 Conductivity Meter (MeterLab) with an Amel standard cell (platinum electrodes). The temperature was controlled by a Haake DC50 K40 thermocryostat with an accuracy of 0.1 °C. Samples were thermostated for 1 h before every measurement. Thermal weight loss temperature was detected with a TA Instruments Q50 thermogravimetric apparatus. Every sample was heated from room temperature to 500 °C at the scan rate of 10 °C/min under argon flow. The instrument sensitivity is of 0.1 µg.

### 2.2. Electrochemical study

ORR in different electrolytes was investigated by cyclic voltammetry at glassy carbon electrode (GCE, 3 mm diameter) in a 5 mL cell that was thermostated at 30 °C by a Huber CC304 thermostat. The GC was polished with alumina paste on a Selvyt cloth before each scan, except for the stability test when the experiments were run continuously. A Li counter electrode (separated from the solution by a porous frit) was used while the reference electrode was a silver wire in 6 × 10<sup>-2</sup> M AgTFSI (97%, Aldrich)-PYR<sub>14</sub>TFSI; the reference electrode potential was checked vs. lithium and the working potentials are reported vs. the Li<sup>+</sup>/Li couple. Oxygen (>99.999%, SIAD) was bubbled through the cell for at least 30 min before starting the analyses and was continuously flowed during the experiment. The electrochemical tests were performed with a PerkinElmer VSP multichannel potentiostat/galvanostat. The voltammetric scans were corrected for the uncompensated resistance which was evaluated by electrochemical impedance spectroscopy at 10 kHz.

Galvanostatic measurements were performed with carbon paper (CP, Spectracarb 2050, Spectracorp, 0.5 cm<sup>2</sup>) working electrodes dried under vacuum at 120 °C overnight before use. During the measurement, the electrolyte was stirred and continuously fed with O<sub>2</sub>.

### 2.3. Oxygen solubility by luminescence lifetime analysis

Oxygen solubility in LiTFSI-TEGDME electrolytes was evaluated by using tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 99.95%, Aldrich) as a probe [25,26]. This very well-known metal complex presents a luminescence centred at 610 nm (in water), with a metal to ligand charge transfer (MLCT) and triplet character. The luminescence intensity and lifetime are largely affected by the presence of molecular oxygen in solution that acts as a quencher [27,28]. If luminescence quenching is purely diffusional, the luminescence lifetime (and intensity) is determined by the quencher concentration following a relation quantitatively expressed by the Stern-Volmer equation (Eq. (1)) [29]:

$$\frac{\tau}{\tau_0} = 1 + k_q \tau_0 [\text{O}_2] \quad (1)$$

where  $\tau$  and  $\tau_0$  are the lifetime of the luminophore in presence and absence of the quencher, respectively, and  $k_q$  is the quenching constant. Quenching is strongly influenced by diffusion of the

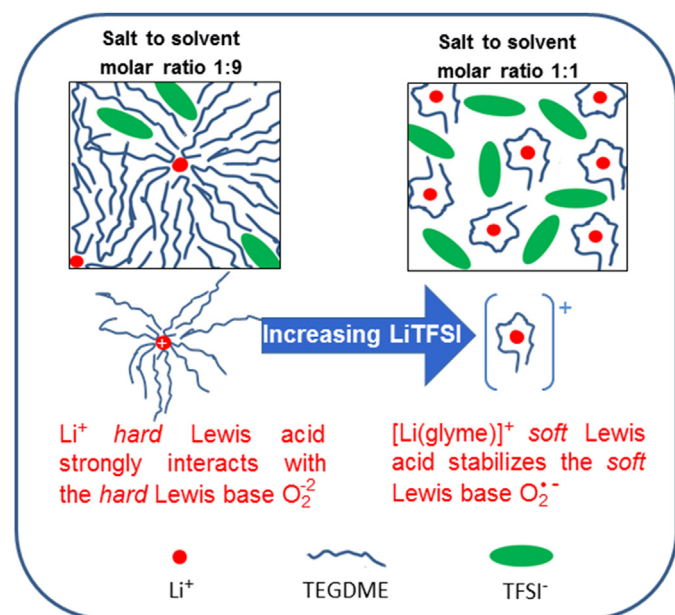


Fig. 1. Schematic representation of LiTFSI-TEGDME solutions. On the left, a diluted solution; on the right, an equimolar solution with an IL-like structure.

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