

Stability of electrolyte solutions for non-aqueous Li-O₂ cells and effect of impurities on cell cycling behavior

K. Uta Schwenke, Stefano Meini, Michele Piana, Juan Herranz, Hubert A. Gasteiger

Technische Universität München,
Lichtenbergstr. 4, D-85748, Garching, Germany

E-Mail: uta.schwenke@tum.de

Lithium-air batteries are considered as highly promising electrical energy storage devices for electric transport application principally due to the large theoretical specific capacity of the oxygen cathode. Energy densities approximately 3-fold larger than the 200 Wh·kg⁻¹ currently envisaged for fully-packaged Li-ion batteries [1] would allow their application in long-range full-electric vehicles. However, numerous issues related to discharge and charge mechanisms need to be solved before commercialization.

The search for stable electrolyte systems is still one of the main tasks in Li-air battery research as up to now none has provided truly reversible oxygen chemistry with the commonly employed carbon-based cathodes [2]. Besides low viscosity and high oxygen solubility for sufficient O₂ supply, the desired properties of a good electrolyte solution are anodic stability at high potentials, passivation or protection of the lithium anode and stability versus oxygen reduction reaction intermediates (e.g., superoxide anion radicals (O₂^{•-})) produced upon discharge at the cathode [3]. To understand the different reactivity issues independently, model systems are needed. Our group developed recently a method based on rotating ring disc electrode voltammetry to quantify the stability of electrolyte solvents against O₂^{•-} [4]. However, this method applies only to highly reactive solvents with large reaction rate constants of O₂^{•-}, so that we investigated further the long term reactivity of O₂^{•-} with different solvents currently employed in Li-O₂ cells via UV-visible spectroscopy. Employing KO₂ as superoxide radical source allowed to study the reaction kinetics of O₂^{•-} independently of other processes occurring during cell cycling. Further, reaction products of KO₂ in contact with the solvents were identified by ¹H NMR and FTIR spectroscopy [5].

We confirm that solvents of the glyme series are sufficiently stable against superoxide radical attack to be used for Li-O₂ battery electrolyte. Discrepancies in the literature with regards to the stability of glymes towards O₂^{•-} were clarified by comparing as-received with distilled tetraglyme. Impurities remaining in tetraglyme from the production process are highly reactive towards O₂^{•-} so that a rapid decay of the radical concentration in contact with as-received tetraglyme was observed in the UV-Vis spectra compared to stable radicals in contact with distilled tetraglyme (Figure 1a). Further, the influence of those impurities was investigated during cell cycling. Consistently with other electrolyte solution components reactive towards O₂^{•-} as organic carbonates (e.g., propylene carbonate) or water [6], we also observed an enhancement of the first discharge capacity of Li-O₂ cells when employing an electrolyte based on impure, as-received tetraglyme (Figure 1b).

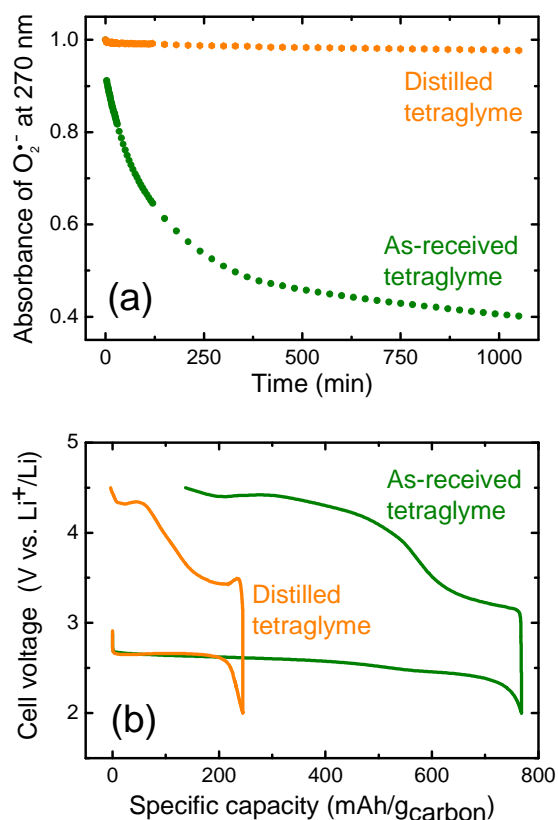


Figure 1: (a) Plot of the absorbance at 270 nm versus time of KO₂ dissolved in DMSO after addition of as-received and distilled tetraglyme, (b) first discharge-charge cycle between 2.0 and 4.5 V at 120 mA/g_{carbon} of Li-O₂ cells using a Vulcan carbon cathode and as electrolyte 0.2 M LiTFSI in as-received and distilled tetraglyme.

However, the cycling behavior of Li-O₂ cells using pure glymes does not differ any more from impure electrolyte solutions from the third cycle on. Furthermore, even after the first discharge in a distilled tetraglyme-based electrolyte, decomposition products are observed in the cathode by NMR and FTIR. The stability against O₂^{•-} is therefore only the first step in the search of a suitable electrolyte. The electrolyte solution of a rechargeable Li-O₂ battery cell has also to be stable against autooxidation in oxygen and against electrooxidation, especially in presence of Li₂O₂.

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