

The role of electrolyte solution solvent stability on the electrooxidation of Li_2O_2 in $\text{Li}-\text{O}_2$ batteries

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The need for sustainable transportation caused by decreasing availability of fossil fuels and global environmental challenges, has triggered the research on high energy density, durable, and low-cost electrochemical energy storage and conversion devices. The theoretically up to 3-fold higher specific energy promised by a fully packaged non-aqueous Li-air battery would allow to overcome EV range limitations due to the maximum achievable specific energy value for high energy Li-ion packs [1].

The charging process of Li-air batteries is not yet fully understood, neither regarding the role of catalysis, nor regarding the intrinsic mechanisms that allow Li_2O_2 crystals poorly connected to the electroactive surface to be quantitatively electrooxidized.

Li_2O_2 -prefilled electrodes are a powerful model system for studying rechargeability and catalysis in Li- O_2 batteries [2,3]. In this work, we explore the rechargeability of Li_2O_2 electrodes based on carbon black and using different electrolyte solutions (0.2 M LiTFSI in DME, diglyme, and $\text{Pyr}_{14}\text{TFSI}$), in order to further understand the mechanisms limiting the O_2 recovery efficiency to a maximum of $\approx 85\%$ [2, 4].

Despite the good reversibility of Li- O_2 cells using $\text{Pyr}_{14}\text{TFSI}$ -based electrolyte solutions demonstrated by our group, only about 10% of the capacity of the Li_2O_2 -prefilled electrode can be obtained. The voltage profile doesn't show a plateau related to Li_2O_2 electrooxidation as with other electrolyte solutions (Figure 1a); furthermore, at potential as high as 5 V_{Li} , minor amounts of O_2 gas are detected by OEMS (Figure 2b), our novel electrochemical mass spectrometry system described in our previous paper [4]. This kind of system shows an interesting trend, whereby the recharge potential of Li_2O_2 electrodes decreases (Fig. 1a) as the electrolyte's anodic stability gets lower (DME < diglyme < $\text{Pyr}_{14}\text{TFSI}$; see Fig. 1b).

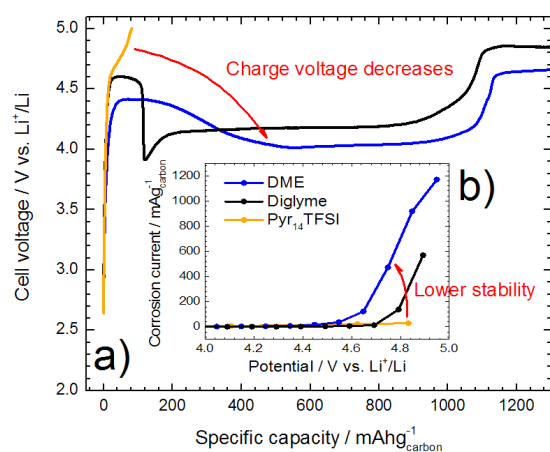


Figure 1: a) comparison between charge voltage profile of Li_2O_2 -prefilled electrodes using different non-aqueous electrolyte solutions: 0.2 M LiTFSI in DME, diglyme, and $\text{Pyr}_{14}\text{TFSI}$; b) comparison between their corrosion currents on a non-catalyzed carbon electrode surface.

The use of a solid, room temperature Li^+ conductor (Ohara, Japan) allowed us to observe a shuttle mechanism in Li- O_2 cells based on glyme electrolyte solutions. When

no physical barrier between anode and cathode is present, overcharging the cell in a galvanostatic mode results in a flat potential plateau at $4.75 \text{ V}_{\text{Li}}$ for diglyme (Fig. 2a, black line); however, no galvanostatic potential plateau is reached up to $5.0 \text{ V}_{\text{Li}}$ when anode and cathode compartments are separated (Fig. 2a, green line). We believe that electroactive species produced from glyme electrooxidation at the cathodic surface (initial potential peak) can serve as redox mediator such as LiI [5] (Fig. 2a, magenta line), enabling the complete electrooxidation of relatively big Li_2O_2 crystals at relatively low overpotentials. Due to the much higher stability of $\text{Pyr}_{14}\text{TFSI}$ compared to glymes, the above conditions cannot be achieved, and Li_2O_2 particles can be only partially oxidized (Fig. 2, yellow lines).

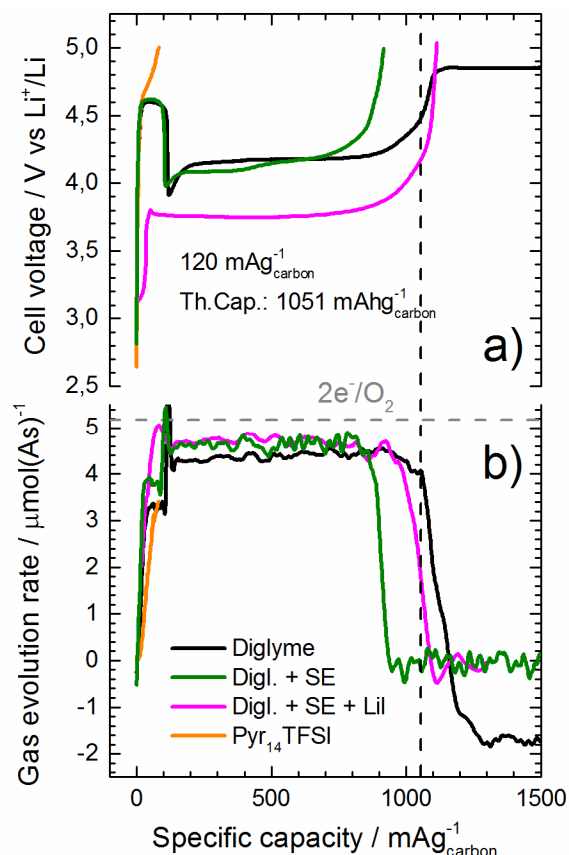


Figure 2: a) comparison between charge voltage profile of Li_2O_2 electrodes using different non-aqueous electrolyte solutions: 0.2 M LiTFSI in diglyme, diglyme with added redox mediator (LiI), and $\text{Pyr}_{14}\text{TFSI}$; SE stands for "Solid Electrolyte" and refers to an Ohara Li^+ conductive glass b) O_2 evolution rate as detected by OEMS.

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