



# Operando UV-visible spectroscopy evidence of the reactions of iodide as redox mediator in Li–O<sub>2</sub> batteries



I. Landa-Medrano<sup>a</sup>, M. Olivares-Marín<sup>b</sup>, R. Pinedo<sup>a,1</sup>, I. Ruiz de Larramendi<sup>a</sup>, T. Rojo<sup>a,c</sup>, D. Tonti<sup>b,\*</sup>

<sup>a</sup> Departamento de Química Inorgánica, Universidad del País Vasco (UPV/EHU), Paseo de las Universidades 7, Vitoria-Gasteiz, Spain

<sup>b</sup> Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB Bellaterra, Barcelona, Spain

<sup>c</sup> CIC Energigune, Albert Einstein 48, 0150, Miñano, Spain

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## ABSTRACT

We monitored by means of UV-visible spectroscopy the formation and consumption of triiodide ion (I<sub>3</sub><sup>-</sup>), generated when iodide ion (I<sup>-</sup>) is used as redox mediator in lithium–oxygen batteries. Results evidence the initial formation of I<sub>3</sub><sup>-</sup> during oxidation, and its decomposition during reduction. Correlation of absorbance with capacity is consistent with the mediation of peroxide oxidation above 3 V. Decrease of I<sub>3</sub><sup>-</sup> absorbance and the appearance of a peak at a wavelength of 410 nm after 14 hours at open circuit voltage revealed side reactions associated to electrolyte degradation leading to the formation of HOI. This work shows that UV-visible spectroscopy is a valuable tool for following reactions involved in the operation of lithium–oxygen batteries based in the absorbance of the species formed or consumed.

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## 1. Introduction

Rechargeable lithium–oxygen batteries (LOBs) have become of increasing interest due to their high theoretical gravimetric energy density of ~3500 Wh/kg [1]. However, many challenges such as high charge overpotential and poor cycling performance still remain unsolved. Actually, these two drawbacks have been demonstrated closely interrelated, as high overpotential during charge is believed to be responsible for degradation reactions of electrolytes and carbon-based electrodes, leading to a gradual capacity fade [2–5]. Charge reaction concerns the oxidation of the discharge product lithium peroxide, in a process known as oxygen evolution reaction (OER):



In order to reduce the mentioned overpotential and minimize side reactions, a large number of catalytic systems have been proposed [6–10]. Nevertheless, redox mediators have lately gained interest as liquid-phase OER catalysts. These redox mediators (RM) are readily oxidized at the oxygen electrode during charge. The oxidation product formed (RM<sup>+</sup>) can diffuse and efficiently oxidize the poorly electronic conductor Li<sub>2</sub>O<sub>2</sub> accumulated on carbon surface. As a result, O<sub>2</sub>, Li<sup>+</sup>, and the initial RM reduced state are regenerated. As far as we know,

tetrathiafulvalene (TTF) [11], iron phthalocyanine (FePc) [12], 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) [13], and iodide (I<sup>-</sup>) [14–17] have been proposed as redox mediators for nonaqueous LOBs, being I<sup>-</sup> the most widely studied. However, a complex chemical interaction between iodide and electrolyte has been recently demonstrated by Kwak et al., including the formation of side products [17].

Herein, we give evidence of the reactions related to the use of iodide (I<sup>-</sup>) as redox mediator in LOBs by *in situ* monitoring the formation and elimination of iodide species by means of UV-visible spectroscopy. This tool is particularly useful when the electrochemical reactions involve species that absorb visible light as is often the case for redox mediators and their side products.

## 2. Experimental

Electrochemical measurements were carried out in the homemade cell described in Fig. 1. Indium Tin Oxide (ITO, PSiOTec, Ltd., UK) 5 Ohm/square coated glass (Polished sodalime with SiO<sub>2</sub> barrier layer) was used as oxygen electrode and a piece of Li foil (Sigma-Aldrich, 0.4 mm thick) pressed on the stainless steel tube used to introduce oxygen to the solution was used as anode. Electrolyte (1.7 mL volume) consisted of 1 M LiTf (Sigma-Aldrich) and 0.1 M KI (Sigma-Aldrich) dissolved in TEGDME (≥99%, Sigma-Aldrich) prepared in a glovebox without exposure to air. All the materials were dried prior to their introduction to the glovebox, where the cell was assembled. After assembling, the cell was purged with dry oxygen for 30 seconds. Electrochemical tests were conducted using a Biologic VMP3. Cyclic

\* Corresponding author. Tel.: +34 935 801 853X362.

E-mail address: [dino.t@csic.es](mailto:dino.t@csic.es) (D. Tonti).

<sup>1</sup> Present address: Physikalisches-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany.

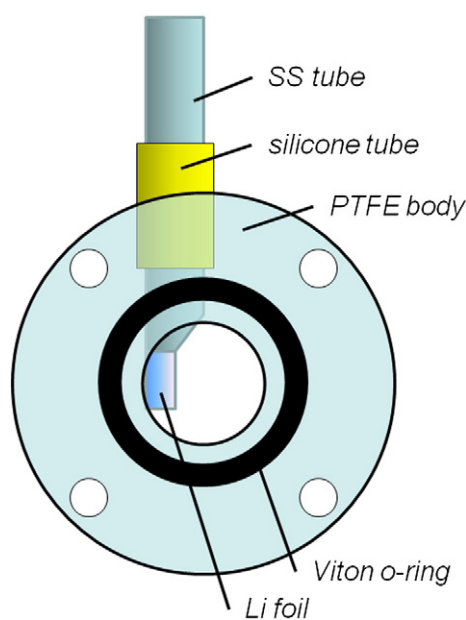


Fig. 1. Schematic representation of the cell used for the *in-situ* UV-visible spectroscopy.

voltammetry (CV) measurements were carried out at a scan rate of  $5 \text{ mV s}^{-1}$  between 1.5 and 4.5 V.  $\text{I}_2$  (Aldrich, 99.999%) solution in TEGDME was prepared following the same method. UV-visible spectroscopy measurements were carried out using a Varian Cary 5 two double beam UV-Vis-NIR spectrophotometer. Scans were repeated every 60 seconds in the wavelength range between 350 and 550 nm.

The cell consisted of a ring-shaped polytetrafluoroethylene (PTFE) piece with a small lateral orifice, used to insert a stainless steel tube used to both lead oxygen to the electrolyte and electrical contact to the lithium metal anode. Both sides of the central aperture were closed by glass windows, one of them coated with indium-doped tin oxide (ITO), which was used as oxygen electrode. ITO has also been suggested as an alternative to carbon in LOBs [18]. The electrolyte consisted of 1 M lithium trifluoromethanesulfonate (LiTf) and 0.1 M potassium iodide (KI) in tetraethylene glycol dimethyl ether (TEGDME).

### 3. Results and discussion

The CV curve and the absorbance spectra collected at different stages of the experiment are shown in Fig. 2.

During the cathodic scan, a reduction process could be appreciated starting at 2.25 V, which can be ascribed to oxygen reduction reaction (ORR) (Fig. 2a). This potential was lower than the typically reported 2.6–2.7 V when carbon-based oxygen electrodes are used and can be related to the poor electronic conductivity of ITO compared to carbon [17] and to the low surface area of these flat electrodes. At OCV, an absorbance peak with a maximum at 365 nm could be observed, which is typical for  $\text{I}_3^-$  [19]. The presence of this peak could be attributed to the reaction between  $\text{I}^-$  and trace amounts of hydrogen peroxide in TEGDME, which is a common product formed during glyme storage [20]:



Yin et al. also reported the presence of this peak before charging their NaI-containing sodium–oxygen battery [21]. Based on this reaction, it can be deduced that  $\text{H}_2\text{O}$  and  $\text{I}_3^-$  would be chemically formed. From the extinction coefficient in ref. [18], we estimate a  $\text{I}_3^-$  concentration of about  $4 \cdot 10^{-5} \text{ mol/L}$ , two orders of magnitudes less than the  $\text{I}^-$  present in solution.

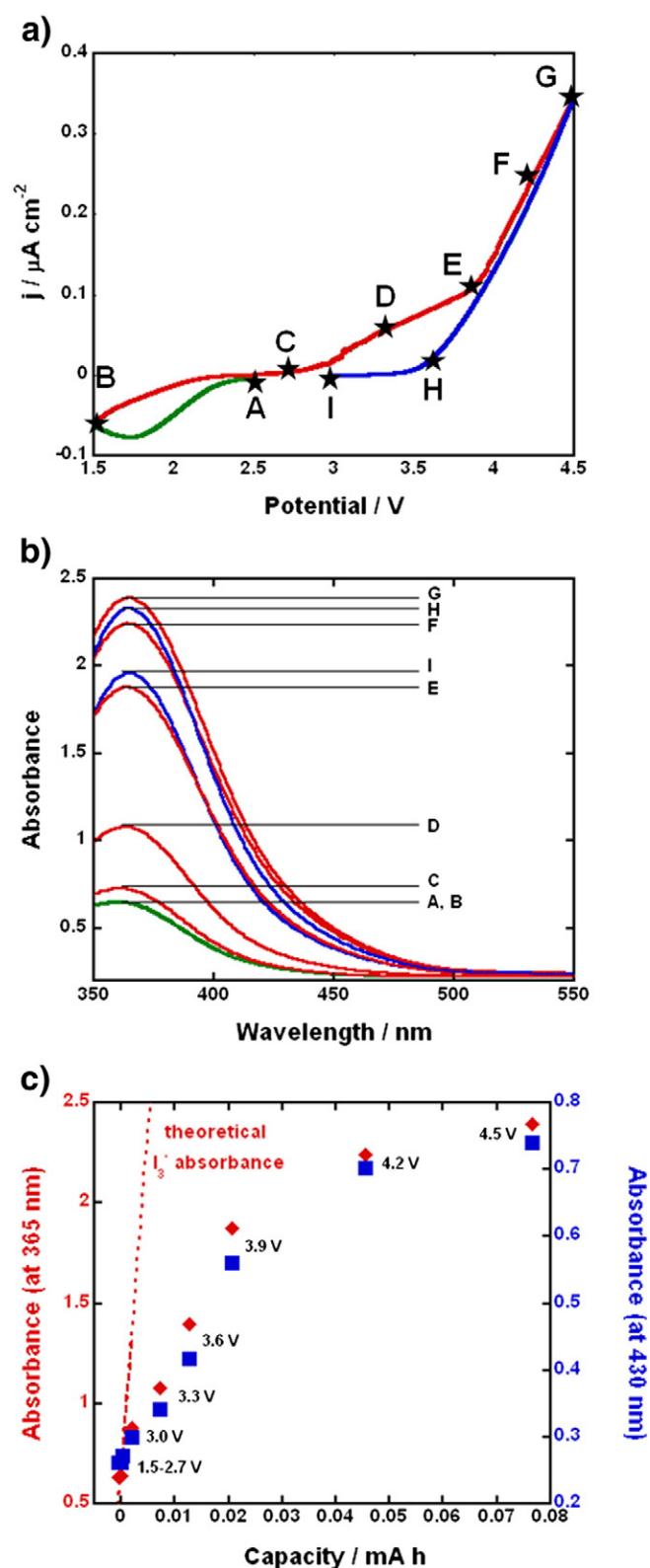


Fig. 2. (a) Cyclic voltammetry carried out at a scan rate of  $5 \text{ mV s}^{-1}$  between 1.5 and 4.5 V. Blue stars correspond to the stages of the voltammetry for which the absorbance spectra is shown in panel b. (b) The absorbance spectra collected with the UV-vis spectroscopy at different stages of the cyclic voltammetry. (c) Absorbance values recorded at 365 nm (red diamonds) and at 430 nm (blue squares) vs. capacity of the cell during charge of the cell. Cell potential is indicated for each point and the dotted red line shows the theoretical absorbance at 365 nm.

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