Supporting Information

Organic radicals for the enhancement of oxygen reduction reaction in Li-O₂ batteries

A.Y. Tesio,^{a,b†} D. Blasi,^{a,c†} M. Olivares-Marín,^a I. Ratera,^{a,c*} D. Tonti,^{a*} and J. Veciana^{a,c}

a. Institut de Ciència de Materials de Barcelona-Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus de la UAB, E-08193 Bellaterra, Barcelona, Spain
b. Grupo de electroquímica molecular, INQUIMAE, Departamento de Quimica Inorganica, Analitica y Quimica Fisica, Facultad de Ciencias Exactas y Naturales, Pabellon 2, Ciudad Universitaria, AR-1428 Buenos Aires, Argentina
c. CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Bellaterra, 08193 Barcelona, Spain.
† Authors equally contributed

* Corresponding authors. E-mails dino.t@csic.es; iratera@icmab.es

1. Electrode preparation

The electrodes consisted of a layer of commercial carbon black (SuperP, M.M.M. Carbon) supported on a stainless steel mesh (AISI 316, 180 mesh per inch, ADVENT Research Materials Ltd). Super P (90 wt. %) was mixed with 10 wt. % of polyvinylidene fluoride (PVDF) as a binder in N-methylpyrrolidone (NMP). The slurry obtained was used to impregnate the mesh, which was finally dried at 100 °C for 12 h. The carbon load used was close to 1 mg cm⁻². As a point of interest, Figure S1 shows SEM (left) and TEM (right) images of carbon black Super P. The structure of Super P is composed by a combination of graphitic pseudo-spheroidal nanoparticles (~40 nm) forming a chain-like structure. Strong interconnection of particles form nodules with rounded and irregular contours and generate well-opened and accessible inter-particle structure which produced a wide distribution of pores in the meso and macropore

ranges. Thus, voids with diameter within a wide range of about 20 nm to about 500 nm can be easily observed.



Figure S1.SEM and TEM images of Super P carbon.

2. TTM radical preparation and stability

2.1 Synthesis

TTM radical was synthesized using the procedure reported in literature. ^[1] 1,3,5trichlorobenzene (>99% Sigma-Aldrich), Chloroform (>99.8% stabilized with amylenes Sigma-Aldrich) and Aluminum chloride (Sigma-Aldrich) were used without further purification.

2.2 Electrolyte preparation

A 1 M solution of LiOTf in TEGDME was stored at least 24 h in a mixture of 3 Å and 4 Å dry zeolites (Sigma-Aldrich). The water content, determined by Karl Fisher titration was below 100 ppm. TTM radical was added to a 1 M solution of LiOTf in TEGDME in order to have a concentration of 1 mM. The solution was sonicated for 30 min and then filtered using a PTFE filter of 220 nm.

3. Redox behavior of TTM radical in an ether-based electrolyte

Cyclic voltammetries (CVs) at 20 mV/s were carried out in a standard threeneck flask glass cell where necks were used for the working (Super P electrode), the counter (Pt) and reference (Ag/AgCl 3M KCl) electrodes. Electrochemical tests were done under argon flux using a TEGDME-based electrolyte consisted of LiOTf (Sigma-Aldrich) dissolved in TEGDME (\geq 99%, Sigma Aldrich) (1M) with and without TTM radical (1mM) in a red light room to avoid the radicals damage with light. Figure S2 shows the CVs obtained using aPGSTAT204 AUTOLAB potentiostat.



Figure S2. CVs of Super P electrode containing TEGDME LiOTf (1M) (bottom), TEGDME LiOTf (1M) with TTM radical 1 mM (top) at 20 mV s⁻¹.

4. Electrochemical stability of TTM radical

A chronopotentiometric experiment was carried out with the same conditions and devices used in Section3 in order to analyze the electrochemical stability of the radical. The experiment consisted of applying a constant current of 100 μ A for 30 min to a 1 mM solution of TTM radical in the TEGDME-based electrolyte. The UV-Visible absorption spectrum was obtained before and after electrochemical test using quartz cuvettes with an optical path of 1 mm.

5. Chemical Stability of TTM radical

With the aim to demonstrate possible reactions between anode and TTM-radical, its stability was tested monitoring using UV-Visible Varian Cary 5000 spectrophotometer. A 0.1 mM solution of TTM radical in TEDGME was prepared in the dark and inside a glovebox. Two UV cuvettes were filled with the solution. In one of them some flakes of metallic lithium were added and the solution was sonicated for 5 minutes. Absorption spectra were acquired on both cuvettes during two hours and no changes were observed. Finally, the cap of the cuvette was removed in order to allow the atmosphere to diffuse into the solution. Also in this case the absorption was monitored during two hours and no changes occurred (figure S3).



Figure S3. UV-Visible normalized spectra of TTM solution before and after lithium contact (1 and 2 hours in Ar and then after further 2 hours exposed to the atmosphere).

6. Li-O₂ battery performance

Li-O₂ battery consisted of a Teflon homemade cell based on the Giessen battery design.^[2] Due to the light instability of the radicals in solution,^[3] cells were covered with an aluminum foil in order to keep them in darkness. Electrolyte was 1 M LiOTf (Sigma-Aldrich) dissolved in TEGDME (\geq 99%, Sigma Aldrich) without and with saturated radical and prepared in a glovebox without exposure to air. The separator was a glass fiber filter (filterLab MFV1, 260 µm thick) soaked with ~100 µl of electrolyte, the anode a Li metal foil (Sigma Aldrich, 0.4 mm thick, cut to approx. 0.8 cm²). A nickel foil was used as a current collector. All Li-O₂ cells were assembled in an argon-filled glove box. Once assembled, the cell was purged with pure oxygen for several minutes. Electrochemical tests (CVs at 20 mV/s and of galvanostatic discharges/charges at 0.5 and 0.1mA cm⁻²) were performed using a Biologic VSP multichannel potentiostat at a potential range between of 2.0 and 4.0 V. All tests were done in a lab with

temperature set at 25 °C. As an example, Figure S4 shows the CVs obtained for a Li- O_2 cell with electrolyte saturated with TTM at 20 mV/s under argon and pure O_2 atmospheres. Compared with the CV in the 3-electrode cell (FigureS4) in this case a reversible TTM peak is more evident, even in presence of oxygen. The slow diffusion through the thin electrolyte layer limits the mixing of TTM anion with O_2 molecules within the time scale of the CV scan.



Figure S4. CVs of Li- O_2 battery with ether-based electrolyte saturated with TTM radical under argon (red line) and under pure O_2 (blue line).

7. Detecting the TTM anion using operando UV-Visible technique

The spectroelectrochemical cell described elsewhere^[4] was used to detect the TTM activity. A low TTM concentration was added to the standard TEGDME LiOTf (1M) electrolyte and used in this cell, so that an absorbance of about 0.6 was recorded at 500 nm. Figure S5shows absorption spectra recorded during a galvanostatic discharge and during a galvanostatic charge at 20μ A. The different background is due to the different scattering produced by the deposited Li₂O₂ particles at different stages of their

formation-dissolution cycles. The difference between the spectrum in discharge (reduction) and that in charge (oxidation) is not monotonic, as it would be if only a scattering difference was present. The maximum, observed at 500 nm, is most likely to attribute to the absorption of a small quantity of TTM anion, which presents a relative maximum at the same wavelength.^[5]



Figure S5. Absorption spectra recorded in situ during a galvanostatic discharge and during a galvanostatic charge at 20 μ A using TTM in TEGDME LiOTf (1M) as electrolyte.

REFERENCES

- J. V. O. Armet, C. Rovira, J. Riera, J. Castaiier, E. Molins, J. Rius, C. Miravitlles, S. Olivella, J. Brichfeus, J. Phys. Chem. 1987, 5608-5616.
- [2] C. L. Bender, P. Hartmann, M. Vračar, P. Adelhelm, J. Janek, *Adv. Energy Mater.* **2014**, *4*, n/a-n/a.
- [3] E. G. Marye Anne Fox, Chia-Chung Chen J. Am. Chem. Soc. **1987**, 109, 7088-7094.
- [4] I. Landa-Medrano, M. Olivares-Marín, R. Pinedo, I. Ruiz de Larramendi, T. Rojo, D. Tonti, *Electrochem. Commun.* **2015**, *59*, 24-27.
- [5] J. Veciana, I. Ratera, in *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds* (Ed.: R. Hicks), John Wiley & Sons, Ltd, **2010**, pp. 33-80.