

A gel polymer membrane for lithium-ion oxygen battery



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ABSTRACT

Herein we investigate the use of a gel polymer membrane in a lithium-ion oxygen cell using a nanostructured $\text{Li}_x\text{Sn}-\text{C}$ alloy anode. The gel polymer membrane, studied in terms of ionic conductivity and electrochemical stability, actually enhances the performances of the $\text{Li}_x\text{Sn}-\text{C}/\text{O}_2$ full cell in respect to the bare liquid electrolyte, due to a mitigated oxygen crossover from the cathode to the anode side. Indeed, the protective effect of the gel polymer membrane avoids excessive increase of the interphase resistance, as demonstrated by the study of the time evolution of open circuit voltage and by electrochemical impedance spectroscopy. The use of the gel polymer membrane as well as the replacement of lithium metal by a safe Li-alloying electrode are considered valid strategies suitable for the practical improvement of lithium-ion oxygen battery with increased safety content and enhanced electrochemical performances.

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1. Introduction

High theoretical energy density and low cost represent the principal attracting properties of the lithium oxygen battery that is, therefore, considered the most promising candidate for powering electric vehicles [1–3]. However, the applicability of such as appealing system is limited by several issues, including the poor electrolyte stability and the reactivity of the carbon support with the intermediates formed during the electrochemical process [4–8]. Increasing efforts have been devoted to the improvement of the cell components in terms of stability with the aim to achieve a high performances lithium oxygen battery [9–11]. Among the various solutions, most recently the solid-state and the polymer lithium oxygen systems have shown important potentiality [12–15]. Indeed, the use of solid-state electrolyte media ensures higher safety in respect to the flammable and volatile common liquid solutions that play a key role in view of electric-vehicle application [16,17]. Furthermore, the use of the high-energy lithium metal anode is accompanied by safety concerns associated to its remarkable reactivity, possible dendrite formation during cycling leading to short circuit and thermal runaway [18,19]. The replacement of the lithium metal by alternative lithium-

ion anode material represents one of the possible solutions to this issue [20–22]. Among the various lithium-ion anode, the Li-alloying based materials such as Sn and Si appeared the most promising ones, due to their high theoretical energy density [23–26]. Recent studies revealed that the oxygen crossover from the cathode to the anode side, i.e., a process affecting also fuel cell systems [27,28], may represent a relevant side reaction avoiding future development of the lithium oxygen system [29–32]. The lithium metal can, in fact, react with the oxygen solubilized in the electrolyte at the cathode side to form lithium oxide or hydroxide at the metal surface, thus increasing the cell resistance and polarization and leading, by long term cycling, to possible anode consumption [29–31]. This issue is particularly relevant for cells in which the Li-metal is replaced by alloy-based anodes that is containing limited amount of lithium [22]. Indeed, the fast consumption of the lithium stored at the anode as alloy, by the oxygen dissolved in the electrolyte leads to a rapid cell failure [22], thus suggesting the protection of the anode side as potential solution to achieve high performances lithium-ion oxygen cell. Accordingly, in this paper we investigate a lithium-ion oxygen cell employing a nanostructured $\text{Li}-\text{Sn}-\text{C}$ anode [26] and PVdF-based gel polymer membrane [33] instead of bare liquid electrolyte. The replacement of the lithium metal by alloy anode material ensures high safety, while use of PVDF-based gel polymer membrane partially protects the anode [34] and mitigates the undesired side reaction caused by the oxygen crossover [29]. Despite requiring further improvement, the results reported in this paper represent a first attempt aimed to the achievement of high-energy lithium-ion oxygen cell suitable for application in a new generation of electric vehicles.

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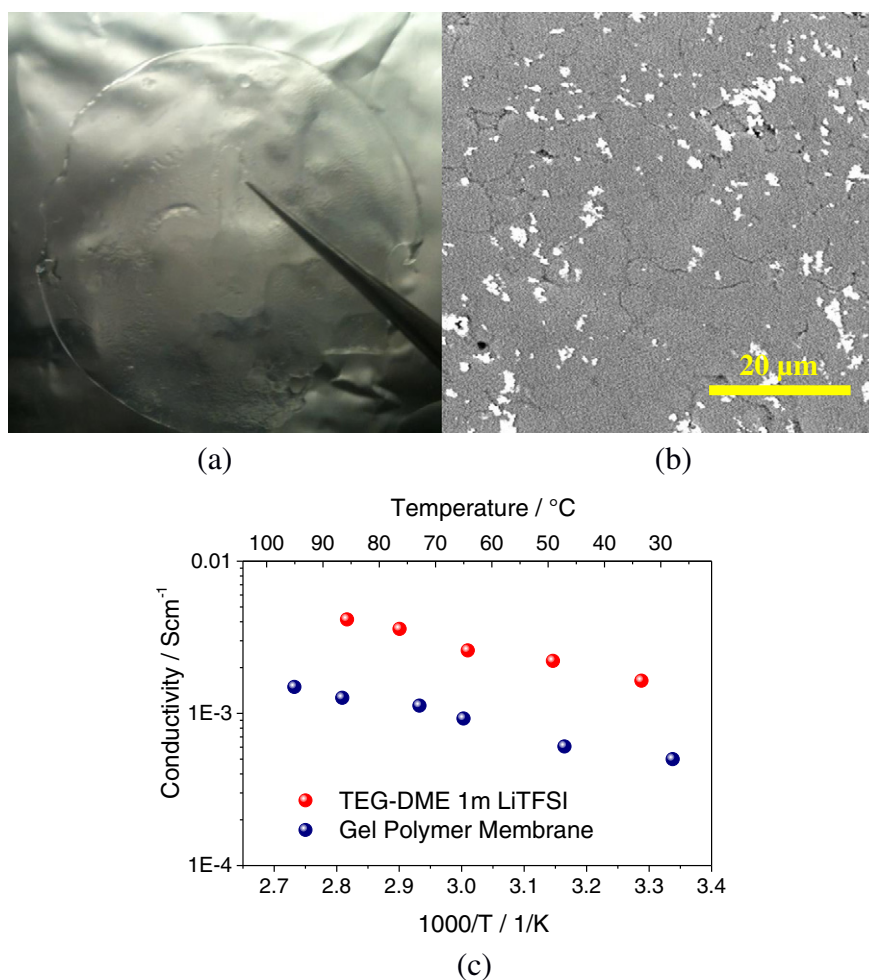


Fig. 1. (a) Photographic image and (b) SEM image of the gel polymer membrane. (c) Arrhenius plots within 25 °C and 95 °C of the of the bare TEG-DME 1 mol kg⁻¹ LiTFSI electrolyte solution (red dot) and of the gel polymer membrane (blue dot).

2. Experimental

2.1. Electrolyte and membrane preparation

The gel polymer membrane was prepared by employing PVDF (6020 Solef Solvay) as polymer matrix, lithium bis(trifluoromethane) sulfonimide (LiTFSI Sigma 99.9%) to allow increased porosity and ensure an efficient swelling process and ZrO₂ nanoparticles (Sigma ~100 nm 99%) ceramic filler employed in order to improve the mechanical proprieties of the membrane, in a PVDF:LiTFSI:ZrO₂ proportion of 80:10:10. The mixture was homogeneously dispersed using as solvent N-Methyl-2-Pyrrolidinone (NMP anhydrous 99.5% Sigma). The dispersion was stirred at 60 °C for 4 h, in order to obtain homogeneous slurry. Following, the viscous slurry was cast onto glass support using a doctor blade. The obtained film was dried at room temperature in open air under the wood for 2 days until a homogenous dry polymer film was achieved due to solvent evaporation. The obtained film, characterized by good mechanical proprieties, was easily removed from the glass support. All the procedures described above were performed in air. The residual solvent and moisture traces were then removed by drying the membrane under vacuum at 110 °C for three days. Before the use in cell, the obtained membrane was swollen for 24 h in a TEG-DME 1 mol kg⁻¹ LiTFSI electrolyte solution, evidencing an electrolyte uptake of about the 78% w:w. The electrolyte solution was prepared using tetraethylene glycol dimethyl ether (TEG-DME 99% Sigma). The TEG-DME solvent was dried employing dry zeolite 4 Å, until a water content

below 10 ppm. The electrolyte was prepared in the 1 mol kg⁻¹ ratio in an argon filled glow box, with a water and oxygen content lower than 1 ppm, using lithium-bis-(trifluoromethanesulfonyl)-imide LiN(SO₂CF₃)₂ as lithium salt (Sigma Aldrich 99.9%).

2.2. Li_xSn-C and GDL-Super C65 electrodes preparation

The Sn-C composite used as anode material was synthesized by a procedure described previously [26,35]. The Sn-C electrode was prepared by casting on a copper foil a slurry composed by 80% active material (Sn-C) 10% Super-C65 (Imerys) and 10% PVDF (6020 Solef Solvay), dispersed in N-Methyl-2-pyrrolidinone (NMP anhydrous, 99.5% Sigma Aldrich). The electrodes were dried at 70 °C in oven, punched as 16-mm disks and finally dried under vacuum at 110 °C overnight, obtaining a loading of about 3–4 mg cm⁻². The Li_xSn-C electrode was formed before the use in lithium-ion oxygen cell by full chemical lithiation following a procedure described in previous papers [20,29, 36], consisting by the direct reaction of the Sn-C electrode with a lithium foil whet by the electrolyte solution, followed by the removal of the lithium foil, washing and final drying under vacuum of the electrode.

The cathode was obtained by using a gas diffusion layer GDL 35 BC (SGL Group) as the support. The electrode was formed by casting a slurry composed by 80% Super-C65 (Imerys, surface area of about 62 m² g⁻¹) and 20% PVDF (6020 Solef Solvay), dispersed in N-Methyl-2-Pyrrolidinone (NMP anhydrous, 99.5% Sigma Aldrich). The electrodes were dried at 70 °C in oven, punched as 16-mm disks and finally dried

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