



Short communication

Au-coated carbon cathodes for improved oxygen reduction and evolution kinetics in aprotic Li–O₂ batteries



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ABSTRACT

Metal-oxygen systems are an attractive option to enhance the specific energy of secondary batteries. However, their power is limited by the oxygen electrode. In this communication we address the issue of the sluggish kinetics of the oxygen cathode in the aprotic Li–O₂ batteries. The electrochemical performances of newly designed carbon electrodes coated with 50 Å thick Au layer are evaluated and compared with those of unmodified electrodes. Despite the low noble metal content (~2 wt.%), the Li–O₂ batteries built with the abovementioned Au-coated cathodes show considerably enhanced kinetics as demonstrated by the higher onset potentials for the oxygen reduction reaction (~2.6 V at a current rate of 1000 mA g⁻¹), together with reduced oxygen evolution potentials.

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1. Introduction

Aprotic rechargeable Li–O₂ batteries are considered promising candidates for powering next generations of electrical vehicles. Although the theoretical energy density of Li–O₂ batteries is much higher than that of Li-ion batteries, many fundamentals and practical issues hinder the development of such technology of batteries.

The sluggish kinetics of the oxygen cathode in aprotic environments is a well documented issue [1]. As a consequence, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) suffer of high overpotentials. The incorporation of an electrocatalyst in the oxygen cathode might therefore help in overcoming this issue. Although there is a vast literature about the electrocatalysts for both ORR and OER in aqueous media, rare are the studies in organic electrolytes. Earlier studies carried out in lithium-containing carbonate-based electrolytes, which now have been demonstrated to largely decompose under oxygen reduction/evolution conditions [2–6], suggested Au as a good catalyst for the 2-electron reduction of oxygen leading to the formation of lithium peroxides (Li₂O₂) [7,8]. More recently, Bruce and co-workers [9] demonstrated the superior electrochemical performance of nanoporous gold electrodes in Li–O₂ cells containing a DMSO-based electrolyte. Accordingly, Abraham et al. reported that Au electrodes show the ability for high-efficiency recharging of the oxygen electrode in an ionic liquid electrolyte [10]. Nevertheless, the very high weight and cost make electrodes containing between 40 [7,8] and 100 [9,10] wt.% of Au unfeasible for practical application.

In this preliminary study we report a new approach to incorporate low amounts of Au in the final carbon cathodes. For the first time the electrochemical behavior of Li–O₂ cells fabricated with carbon electrodes coated with 50 Å thick Au layer is investigated. Despite the low amount of noble metal (~2 wt.%) in the final composite electrode, we demonstrate improved ORR/OER kinetics of the Li–O₂ batteries containing LiTFSI-tetraglyme as the electrolyte and the Au-coated carbon cathodes.

2. Experimental

Tetraglyme was purchased from Aldrich and dried first over molecular sieve and then vacuum-dried at 80 °C. Bis(trifluoromethane) sulfonimide lithium (LiTFSI) salt (Aldrich) was also vacuum-dried before being used. The 1 M LiTFSI/tetraglyme electrolyte was prepared and stored in an Ar-filled glovebox (MBrown) where the O₂ and H₂O levels were kept below 0.1 ppm. The carbon cathodes were prepared by coating a suspension of carbon, Super-P (Timcal) or KetjenBlack EC-600JD (Akzo Nobel), and PvdF (Aldrich) in NMP (mass ratio carbon: PVDF 8:2) on Gas Diffusion Layers (teflonized Toray paper). Electrodes (Ø12 mm) were then cut and dried at 130 °C under vacuum. The loading of all the electrodes was of 1 mg cm⁻². The two different carbons have been selected due to their differences in surface area and pore volume (KetjenBlack EC-600JD: BET surface = 1410 m² g⁻¹; total pore vol. = 2.06 cm³ g⁻¹/Super-P: BET surface = 69 m² g⁻¹; total pore vol. = 0.14 cm³ g⁻¹) [11].

The 50 Å thick gold coating was obtained by magnetron sputtering of a gold target using argon gas based plasma. An EMITECH K350 attached to a K950x sputter coater was employed for this purpose. The stage containing the electrodes was rotated slowly during sputtering to

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ensure uniform deposition and the amount of deposition was monitored using an in-built quartz-crystal microbalance.

A Zeiss dual-beam NVISION 40 was used for scanning electron microscopy. The operating voltages for imaging and spectroscopy were 5 kV and 20 kV respectively. The images were acquired using a secondary-electron detector with an in-lens configuration. The energy-dispersive X-ray spectra (EDX) were acquired using EDAX (Ametek Inc.) attachment mounted on the SEM.

The electrochemical performance of the manufactured electrodes has been evaluated by assembling coin-cells having the top drilled with seven holes ($\varnothing 1.3$ mm), which allowed O_2 to get into the system. A lithium disk acted as the counter electrode, 1 M LiTFSI/tetraglyme as the electrolyte and Whatman glass fiber as the separator. Once assembled, cells were sealed in a glass tube provided with electrical connections and inlet and outlet for O_2 purging.

Electrochemical measurements have been carried out using a Versastat4 (Princeton Applied Research). All potentials reported hereafter are given vs. the Li^+/Li couple. All current densities are given as $mA\ g^{-1}$ and/or $mA\ cm^{-2}$, whereas capacities are expressed as $mAh\ g^{-1}$. The normalization to the mass has been calculated on the basis of the weight of carbon or of Au/carbon in the electrodes.

3. Results and discussion

The SEM micrographs of Fig. 1a–b show the morphology of the unmodified and Au-coated Super-P based electrodes respectively. Both the images were obtained using 5 kV primary electron beam and in-lens secondary electron detector. The scale bars correspond to 200 nm. The morphology of the unmodified electrode is smooth whereas for the case of the Au-coated electrode, it is grainy, consistent with the presence of Au-nanoparticle coating. The evidence of the deposition was also noticeable optically because of the shiny nature of the post-deposition electrodes. It can also be observed that the Au-coating is rather uniformly distributed due to the sample-stage rotation during the sputter deposition process. Very similar micrographs have been obtained for the KetjenBlack ones (not shown for the sake of brevity). During sputter deposition, the sputtered atoms are ejected from the target material (Au) and deposited on the porous carbon

electrode. Considering that the pore size of the electrode is 3 orders of magnitude larger than the sputtered atoms, the variation in the electrode porosity before and after deposition is negligible. Also the thickness of the cathodes ($30 \pm 1\ \mu m$, Toray paper excluded) is not influenced by the Au-coating. Furthermore the Au atoms would be expected to permeate at least several micrometers into the electrode further aided by surface diffusion and sample stage rotation during deposition. However, shadowing effects will ultimately limit the reachable depth for coating.

Fig. 1c–d shows the EDX spectra from uncoated and Au-coated electrodes. The presence of Au in the latter case is evident from the corresponding peak seen in Fig. 1d. The F peak seen in both the cases arises due to the PvdF binder. Trace amounts of oxygen signal is also present in both the cases.

Fig. 2a–b shows the galvanostatic discharge curves collected at various current densities of Li– O_2 cells fabricated with unmodified and Au-coated Super-P cathodes. The discharge capacities have been limited at $500\ mAh\ g^{-1}$. The use of such modified protocol avoids the formation of Li_2O at the cathode side while assuring that of Li_2O_2 [12–14]. At low C-rates ($\leq 200\ mA\ g^{-1}$), unmodified Super-P electrodes (Fig. 2a) show flat discharge plateaus and achieve the full capacities. We here note that the electrochemical performance of the Li– O_2 cells fabricated with the unmodified Super-P electrodes is comparable with those found in literature where typical current densities range from 25 to $150\ mA\ g^{-1}$ [9,12–14]. Nevertheless, Au-coated Super-P electrodes show higher plateau potentials (e.g. $\sim 100\ mV$ at $200\ mA\ g^{-1}$) than those of unmodified ones. As already demonstrated, the discharge plateau is due to the 2-electron reduction of O_2 with the consequent formation of Li_2O_2 [12–14]. The higher discharge potentials of the Au-coated electrodes can be therefore ascribed to increased ORR activity due to the presence of the Au catalyst. Increase of the discharge rate results in the increase of the overpotential. As a consequence, at a current density of $300\ mA\ g^{-1}$ the discharge curves of pure Super-P cathodes appear sloped and the maximum capacity achieved is well below $500\ mAh\ g^{-1}$. Conversely, due to the improved ORR kinetics Au-coated ones (Fig. 2b) retain flat plateaus at every current rate and achieve full capacities. It is worth noting that the remarkable lower overpotentials observed for the Au-coated electrodes in respect to those of unmodified

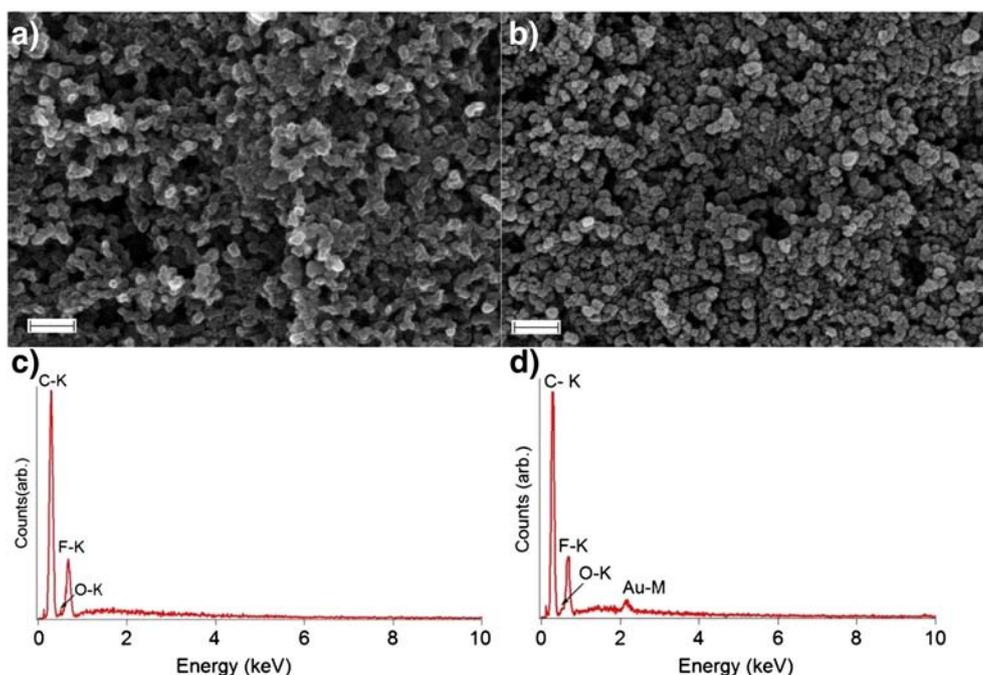


Fig. 1. SEM micrographs and EDX spectra for unmodified (a, c) and Au-coated (b, d) Super-P based cathodes. The scale bar corresponds to 200 nm.

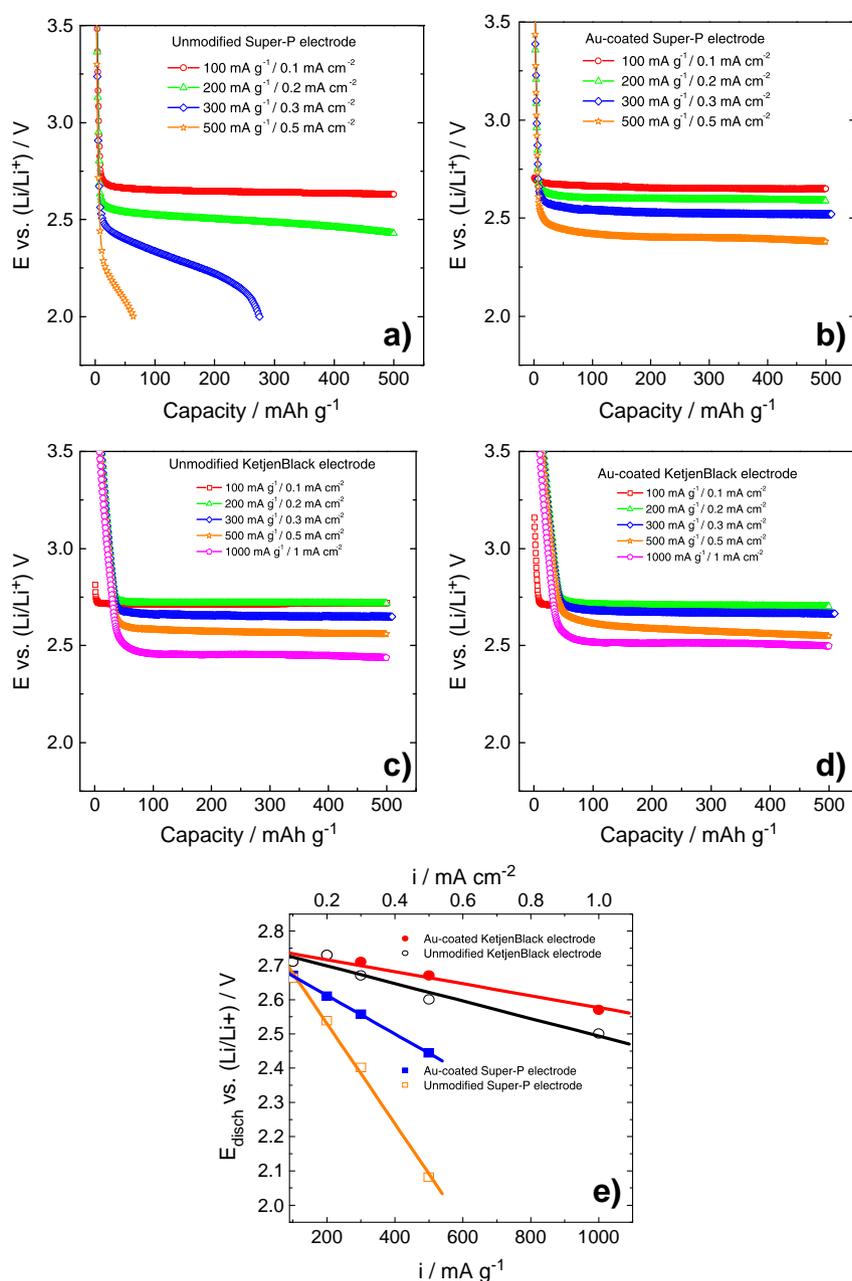


Fig. 2. Galvanostatic discharge curves collected at various current densities, expressed as mA g⁻¹ or mA cm⁻², of Li-O₂ cells with Au-coated and unmodified Super-P (a, b) or KetjenBlack (c, d) cathodes. e) Onset ORR potentials vs. applied current densities for unmodified and Au-coated KetjenBlack and Super-P electrodes.

ones are maintained over the entire discharge, which in agreement with previous results [7], suggest that the 2-electron reduction of oxygen is catalyzed by Au during the entire process.

In order to confirm the efficacy of the Au coating in improving the electrochemical performance of the oxygen cathodes, we evaluated and compared the electrochemical behavior of electrodes manufactured with a different type of carbon. Fig. 2c–d shows the galvanostatic discharge curves for Li-O₂ batteries with unmodified and Au-coated KetjenBlack electrodes. The higher surface area than Super-P together with the high pore volume of KetjenBlack [11] is beneficial for the battery performance. This is probably due to enhanced reaction rates per gram of carbon and easier accommodation of the solid Li₂O₂ particles generated during discharge. The comparison of the results obtained for Au-coated and unmodified KetjenBlack electrodes confirms those reported for Au-coated and unmodified Super-P ones. Indeed, we note that the Au-coated KetjenBlack cathodes allow the Li-O₂ cells to be

discharged up to a rate of 1000 mA g⁻¹ with a discharge plateau >2.5 V, which corresponds to a 60 mV higher potential than that of unmodified ones.

To further assess catalytic activity of the Au-coating before significant self-poisoning, we extrapolated from the galvanostatic curves of Fig. 2a–d the ORR onset potentials at discharge capacities of ~50 mAh g⁻¹ and plotted as a function of the applied current density. As Fig. 2e shows, higher initial discharge potentials are found for Au-coated electrodes, thus clearly demonstrating higher ORR activity relative to unmodified carbon ones.

We finally investigated the electrochemical behavior of Au-coated and uncoated cathodes under oxygen evolution conditions. Fig. 3a depicts the galvanostatic charge curves (current density 50 mA g⁻¹) of Li-O₂ batteries with bare and Au-coated Super-P and KetjenBlack electrodes, which followed a discharge step carried out at 200 mA g⁻¹ with capacity limitation of 500 mAh g⁻¹. In either case, lower average

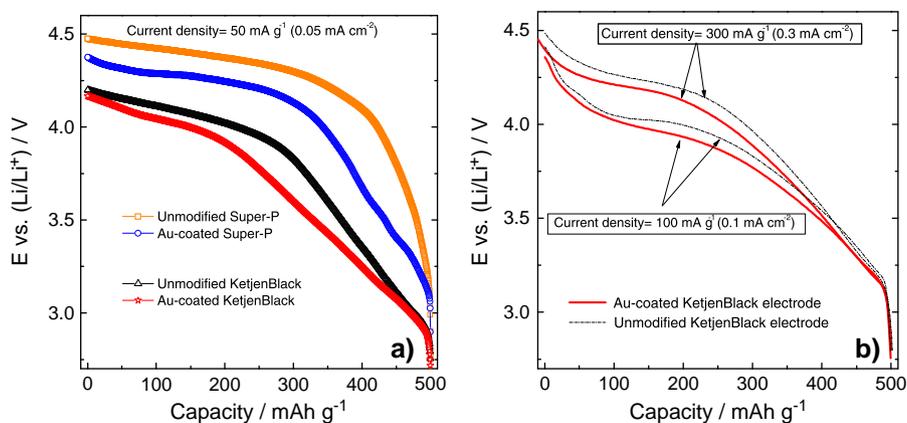


Fig. 3. a) Galvanostatic charge curves, collected at 50 mA g^{-1} (0.05 mA cm^{-2}) of unmodified and Au-coated Super-P and KetjenBlack electrodes. b) Comparison of galvanostatic charge profiles of unmodified and Au-coated KetjenBlack electrodes collected at current densities of 100 and 300 mA g^{-1} corresponding to 0.1 and 0.3 mA cm^{-2} , respectively.

OER potentials are achieved with the Au-coated electrodes, in agreement with previously studies on Au [7,9,10].

Since KetjenBlack-based cathodes outperformed Super-P based ones, we further investigated and compared the OER of the Au-coated and bare KetjenBlack electrodes by means of galvanostatic experiments carried out at increased current densities. The comparison of the obtained curves, reported in Fig. 3b, clearly demonstrates the effectiveness of the Au-layer in improving the OER kinetics, which translates into lower average charge potentials.

4. Conclusions

In this preliminary study we reported a novel route to incorporate low amounts of Au in the air cathodes for aprotic Li-O_2 cells. We demonstrated that despite the low noble metal content ($\sim 2 \text{ wt.}\%$) in the final electrode, the Au-coated carbon cathodes outperform those uncoated in terms of improved ORR/OER kinetics. Our results also suggested that the use of the KetjenBlack carbon, which has higher surface area than Super-P, is beneficial for the cell performance. As a result, the Li-O_2 cells manufactured with the Au-coated KetjenBlack cathodes can be discharged at comparatively high current (1000 mA g^{-1}) with small overpotential and show decreased charge potentials. Further studies are in progress to investigate the long-term cycling stability of the Li-O_2 cells manufactured with the Au-coated electrodes.

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