



Silver nanowires as catalytic cathodes for stabilizing lithium–oxygen batteries



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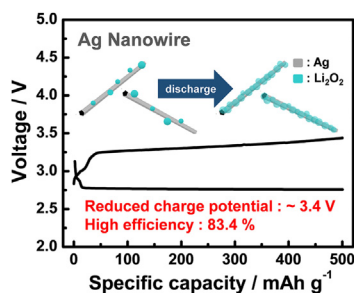
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HIGHLIGHTS

- Ag nanowires proven as a catalytic cathode material for Li–O₂ batteries first time.
- Li–O₂ cells with AgNW cathodes exhibit low over-potential for OER.
- Li–O₂ cells with AgNW cathodes allow high specific discharge capacity.
- Li₂O₂ is deposited on AgNW cathodes in unique morphology.
- Unique morphology of Li₂O₂ precipitation promotes excellent performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanowires have been investigated as a catalytic cathode material for lithium–oxygen batteries. Their high aspect ratio contributes to the formation of a corn-shaped layer structure of the poorly crystalline lithium peroxide (Li₂O₂) nanoparticles produced by oxygen reduction in poly-ether based electrolyte solutions. The nanowire morphology seems to provide the necessary large contact area and facile electron supply for a very effective oxygen reduction reaction. The unique morphology and structure of the Li₂O₂ deposits and the catalytic nature of the silver nano-wires promote decomposition of Li₂O₂ at low potentials (below 3.4 V) upon the oxygen evolution. This situation avoids decomposition of the solution species and oxidation of the electrodes during the anodic (charge) reactions, leading to high electrical efficiency of lithium–oxygen batteries.

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1. Introduction

In order to promote the electro-mobility revolution, it is necessary to increase the driving ranges of electric vehicles. These challenges boost the need for super batteries with ultra-high energy densities. Rechargeable non-aqueous lithium–oxygen (Li–O₂) batteries are promising because they have very high theoretical

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energy densities (3500 Wh/kg and 3400 Wh/L), greater than any lithium-ion battery [1–4]. Unlike Li-ion batteries, Li–O₂ batteries are discharged and charged with lithium peroxide (Li₂O₂) formation and decomposition, respectively [2–6]. All the relevant non-aqueous electrolyte solutions are unstable [7–13] during oxygen reduction reaction (ORR, forming Li₂O₂), and oxygen evolution reaction (OER, decomposing Li₂O₂). Most non-aqueous solvents are susceptible to nucleophilic attacks by reduced O₂ species, which are formed during discharge. Carbon materials also react with oxygen moieties and degrade. Therefore, development of more stable electrolyte solutions and cathode materials is crucial for making Li–O₂ batteries to become a practical system.

In addition, precipitation of Li₂O₂ blocks the cathode's surface during discharging, what terminates the effective electrochemical reaction and limits the capacity [7,8,13,14]. In the charging process, oxidation of the non-conductive Li₂O₂ precipitants may require high over-potentials, in which solution species may be readily oxidized. In order to address these shortcomings, many researchers [15,16] tried to modify the morphology, size, and crystallinity of Li₂O₂ during its generation by electro-catalysis and the use of composite cathodes comprising nano-materials. Carbon-based materials have been the natural materials of choice for the cathodes because they are highly conductive, catalytically effective, and inexpensive [17–19]. Hence, various carbon-based cathode materials have been reported, for example, porous carbon [17], carbon nanotube (CNT) [18], and graphene [19] cathodes. However, carbon can be attacked by reduced O₂ species, which produces Li₂CO₃ [20,21]. Hence, replacing carbon [22,23] or protecting the reactive sites on carbon materials have been suggested as possible solutions [24]. However, we believe these approaches are not the best solutions for Li–O₂ batteries.

Efforts have been made to decrease the over-potential for the formation and decomposition of Li₂O₂ [25–34], by identifying catalysts that can control the morphology of Li₂O₂ [32,33]. Morphological control makes Li₂O₂ easier to decompose on charging. We recently reported that metal oxide hybrid cathodes exhibited better electro-catalytic activity when combined with tetra-ethylene glycol dimethyl ether (TEGDME) based solutions [34]. However, these cathodes required high mass loading and are expensive, negating the advantage of high gravimetric energy density offered by Li–O₂ batteries. In a recent work we discovered that Ag is a better cathode material than carbon for non-aqueous oxygen reduction and evolution [35]. We demonstrated advantages of electrodes comprising silver micro-particles (AgMP). That published work was in fact the starting point for the studies reported in this paper. Herein, we intended to investigate the effect of the morphology of Ag based electrodes in Li–O₂ cells. We show indeed that silver nanowires (AgNW) are better alternative cathode materials for Li–O₂ batteries than carbon and silver micro or nano particles. AgNW greatly reduce the charging over-potential needed for OER at the solution/electrode interface and are more effective than silver nanoparticles (AgNP). AgNW deliver reversible Li₂O₂ formation/decomposition on discharge/charge with an average charging potential of ~3.2 V without detection of electrolyte solution decomposition after 50 cycles. The origin of this better catalytic activity was investigated by high-resolution and energy-filtered transmission electron microscopy (HR- and EF-TEM), high-resolution X-ray diffraction spectroscopy (HR-XRD), and Fourier transform infrared (FTIR) spectroscopy, in conjunction with electrochemical technique. Although polyether based solutions may undergo side reactions in Li–O₂ batteries and their stability is questionable in these systems, it seems that they are still very relevant to these batteries, because they may be the most suitable and the least reactive toward any relevant negative electrodes in these systems. Therefore, we concentrated only in them in the

present work. In the present work, we substantiated further the advantage of silver over carbon as a cathode material in Li–O₂ cells and demonstrate the importance of the morphology of the cathode's surface. Certain nano-structures (AgNW in the present case) enable high specific capacity upon oxygen reduction and promote electro-catalysis for decomposition of Li₂O₂ to oxygen molecular.

2. Experimental

2.1. Synthesis of AgNW

From the various methods for synthesizing AgNW reported in the literature [36–40], we chose a polyol process because it is facile and reliable [40]. As explained in the above cited papers, silver ions are reduced to clusters of silver atoms by ethylene glycol (EG). These clusters evolve into multiply twinned particles via nucleated seeding, stimulated thermally (the reaction temperature is 180 °C). The silver multi-twinned particles are absorbed and deposited on the surfaces of the growing seeds by injecting polyvinylpyrrolidone (PVP) at a controlled rate and temperature. The passivation of the (100) surface of the growing silver nano seeds by PVP causes asymmetrical growth on the (111) surface of the forming nanowires [40]. We provide below details on a typical synthesis. It is clear that the synthetic route we are using can be easily scaled-up. As an example, 2.54 g polyvinylpyrrolidone (PVP) (K30) in 50 mL ethylene glycol were stirred at 500 rpm for 12 h. 35 mg NaCl were added and stirred for 1 h. Ag precursor was prepared by dissolving 0.5 g AgNO₃ in 25 mL ethylene glycol using sonication. The PVP solution was heated to 180 °C, and the Ag precursor solution was injected drop-by-drop over 1 h. The resulting solution was washed with ethanol and doubly distilled water several times using a centrifuge. The precipitate was dried in an oven at 55 °C. The above procedure can be easily repeated for any amount of electrode's material required. For comparison with our synthesized AgNW, silver nanoparticles were purchased from Aldrich (designated AgNP) to examine the relationship between the morphology and the catalytic performance of cathodes for oxygen reduction and evolution reactions.

2.2. Preparation of Li–O₂ batteries

Cathodes were prepared by mixing 80 wt% AgNW (or AgNP) and 20 wt% polyvinylidene fluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP) then coated on a gas diffusion layer (GDL, TGP-H-030 carbon paper, Toray) and dried at 50 °C under vacuum for 24 h. 1.6-cm diameter pieces were cut from the film (0.8 mg/cm² loading) and assembled into an CR2032 coin-type battery with a glass fiber separator (GF/C, Whatman), and lithium foil (thickness, 400 μm). The bottom of the coin was punched with 21 holes with 1 mm diameter for oxygen flow. 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) in tetraethylene glycol dimethylether (TEGDME) was used as the electrolyte. Solvents were stored over 4 Å molecular sieves in an Ar-filled glove box (final water content <10 ppm, determined using Mettler-Toledo Karl-Fischer titration). All battery assembly procedures were done in an argon-filled glove box (water and oxygen contents were less than 0.1 ppm). Before testing, batteries were placed in an oxygen-filled chamber with a pressure slightly higher than 1 atm at room temperature and were stabilized for 1 h.

2.3. Characterization

The electrochemical tests were conducted using VMP3 Biologic Instruments, set for galvanostatic cycling with a current density of 50 mA/g for 10 h and for cyclic voltammetry measurements using

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