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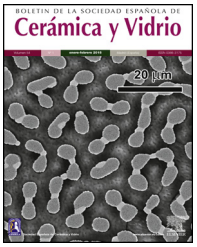

Influence of surface coating on structure and properties of metallic lithium anode for rechargeable Li-O_2 battery

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ABSTRACT

Amorphous lithium phosphorous oxynitride film was coated directly on pre-treated lithium metal as anode of lithium air battery by radio-frequency sputtering technique from a Li_3PO_4 target. The structure and composition of modified anode was analyzed before and after charge/discharge test in a lithium-air battery, which comprises 0.5 M $LiNO_3$/TEGDME as the electrolyte and super P carbon as cathode. Batteries were galvanostatically discharged by an Arbin BT-2000 battery tester between open current voltage and 2.15 V vs. Li^+/Li at various current regimes ranging from 0.1–0.4 mA/cm^2. Compared with fresh lithium, LIPON-coated anode exhibited better electrochemical performance. Good charging efficiency of 90% at a narrower voltage gap with high ionic conductivity of 9.4×10^{-5} S/cm was achieved through optimizing lithium pre-treated conditions, sputtering N_2 flows and suitable solute for electrolyte.

Influencia del recubrimiento superficial sobre la estructura y las propiedades del ánodo de litio metálico para una batería recargable de Li-O_2

Palabras clave:
Pulverización
Ánodo de litio
Batería de aire-litio

RESUMEN

Se realizó un recubrimiento con una capa amorfa de oxinitruro de fósforo y litio (LIPON) mediante pulverización por radiofrecuencia a partir de una diana de Li_3PO_4 directamente sobre litio metal pretratado como ánodo de una batería de litio-aire. La estructura y composición del ánodo modificado se analizó antes y después del ensayo de carga/descarga en una batería de litio-aire que comprende un electrólito de 0,5 M $LiNO_3$/TEGDME y carbono súper P como cátodo. Las baterías fueron descargadas galvanostáticamente por un probador de

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baterías Arbin BT-2000 entre tensión de corriente abierta y 2,15 V frente a Li+/Li a diversos regímenes de corriente que van desde 0,1-0,4 mA/cm^2. En comparación con el litio fresco, el ánodo revestido con LIPON exhibió un mejor comportamiento electroquímico. Se consiguió una buena eficiencia de carga del 90% a un intervalo de voltaje más estrecho con una conductividad iónica elevada de $9{,}4 \times 10^{-5}$ S/cm mediante la optimización de las condiciones del litio pretratado, flujo de N_2 en la pulverización y un soluto adecuado como electrólito.

Introduction

Lithium metal exhibited a lot of advantages as anode in rechargeable batteries owing to its high theoretical capacity and light weight. However, it does not meet the cycle life requirement of rechargeable batteries due to its reactive property with O_2, moisture, CO_2, etc. [1].

In order to improve the stability of lithium, different solid electrolytes, from sulfur based to ceramic electrolytes, including Li_2S–SiS_2 [2], Li_2S–SiS_2–Li_4SiO_4 [3], Li_2S–SiS_2–Li_3PO_4 [4], Li_2S–P_2S_5 [5], and Li_2O–Al_2O_3–TiO_2–SiO_2–P_2O_5 [6] were studied with ionic conductivity in the range of 10^{-3} to 10^{-4} S/cm. Sulfur-based electrolytes are moisture sensitive, they are tend to corrode the deposition equipment and make deposition difficult to handle.

Besides the sulfur-based electrolytes, Li_2S^--based protective layers showed high ionic conductivity [7,8]; however, they are unstable in contact with Li metal anode and also unstable in atmosphere. From a recent report, Li_2O-based LISICONs offer excellent contamination isolation of lithium metal, but their thick/heavy and brittle properties limited battery power density [9,10]. In addition, the brittle nature could potentially result in barrier defects (cracks) upon charge–discharge cycling, leading to parasitic reactions at anode surface [11,12].

As an alternative, amorphous lithium phosphorus oxynitride (LIPON) film formed by sputtering of Li_3PO_4 target in pure N_2, with Li^+ ion conductivity of 2×10^{-6} S/cm at 25 °C [13], has been integrated as an electrolyte layer of thin film battery [14–16]. LIPON as protective layer for lithium air battery was reported [17–20], not directly in contact with lithium anode, but on substrates like Pt [15], LAGP [17], Au, Si [18], etc., or sandwiched with structures $Li_41xTi_5O_{12}$/LIPON/$LixV_2O_5$ [19] using different deposition methods [20]. Al_2O_3 layer was directly deposited on lithium metal by ALD technique [21]. But compared with LIPON, Al_2O_3 layer is not helpful for cycling life improvement. These aforementioned structures have shortcomings like complex and high film resistance and big cell weight, which hinder the energy density. Because the interface between the substrate (Au layer or glass) and LIPON film was neither a perfect contact nor ideally smooth, the electrochemical impedance spectra do not exhibit a pure capacitive response at low frequency [22].

In this study, the LIPON was deposited directly on lithium metal substrate as protective layer; the aim of this study is to investigate a synthesis method for single and efficient modified anode through studying its structure and performances under different deposition conditions in rechargeable lithium air battery.

Experiment

Preparation of lithium metal and Li_3PO_4 target

Lithium discs (Chemetall s.r.l.) were polished gently in Ar gas filled vacuum glove box to get a roughness of around 500 μm. Then, they were subjected to thermal treatment at different temperatures (20–50 °C) for 1–3 h in vacuum furnace to remove the moisture on surface. 1 in. diameter target was prepared by cold pressing of Li_3PO_4 powder (Aldrich, 99.9%) followed by annealing at 630 °C for 12 h and then at 850 °C for 5 h to decompose the PVA binder (1 ml/50 g Li_3PO_4 powder) and prevent any further cracking. The target density is close to 1.9 g cm^{-3}.

Deposition of LIPON

LIPON films were deposited by radio-frequency (rf) magnetron sputtering from a Li_3PO_4 target in a chamber at room temperature, under a nominal radio-frequency power density of 2 W cm^{-2}. The sputtering was performed with a total pressure of 1 Pa under a pure nitrogen atmosphere; the nitrogen flow rate varies from 2 to 40 ml min^{-1}. In order to avoid surface contamination of lithium, all samples were handled in an Ar gas filled glove box and transferred to airtight containers for characterizations.

Lithium air cell assembly

The Li-air battery was assembled in an Ar gas filled dry glove box (Mbraun Labstar) using an ECC-Air electrochemical cell (EL-Cell, GmbH) configuration with openings allowing oxygen to enter the cathode. Lithium disc (Chemetall s.r.l.) with protective LIPON (18 × 0.2 mm) was used as anode while glass fiber (18 × 0.65 mm, ECC1-01-0012-A/L) saturated in an electrolyte was used as separator. A solution of 0.5 M $LiClO_4$ (Aldrich) in tetra (ethylene glycol) dimethyl ether (tetraglyme, Fluka) was used as the electrolyte. As a comparison, 0.5 M $LiNO_3$ (Aldrich) in 1:1 wt/wt TEG-DME was also used due to its proven chemical stability in the presence of Li_2O_2 [23,24]. The cathode was prepared as a thin film over carbon paper GDL (SIGRACET GDL-24BC, SGL Technologies) based current collector. A N-methyl-2-pyrrolidone (NMP) slurry of acetylene black (Shawinigan Black AB50, Chevron Corp., USA) as electronic conductor and poly-(vinylidenefluoride) (PVdF, Solvay Solef-6020) as binder in the weight ratio of 70:30 was deposited over GDL using doctor blade technique [25,26]. The disks of oxygen electrode had an area of 2.54 cm^2. Prior to use, the cathode and modified anode were dried overnight at 55 °C/100 °C,

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