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In situ fabrication of porous graphene electrodes for high-performance lithium–oxygen batteries

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ABSTRACT

These years, Li–O₂ batteries attract wide interest because of its high theoretical energy density. However, the catalytic activity and porous structure of cathode remains a great challenge. In this work, we developed a hierarchical porous graphene foam to serve as a battery cathode, which has much richer active sites for cathodic reaction and channels for Li⁺ transfer and O₂ diffusion. The cathode exhibits a superior specific capacity as high as 9559 mAh g⁻¹ at 57 mA g⁻¹ and remains a high-rate capability of 3988 mAh g⁻¹ at an increased current density of 285 mA g⁻¹. Benefiting from the well-designed cathode structure, the battery can be stably operated for 150 cycles with a stable voltage profile and voltage efficiency up to 65%. The well-designed graphene has a potential to be a superior free-standing cathode to other carbon-based materials due to its good combination of its hierarchical and porous structure, large surface area, abundant defects and excellent mechanical stability.

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Introduction

Due to the rapid depletion of global fossil fuels and increasing pressure of environmental concerns, it is particularly urgent to replace the existing oil-fueled automobiles with hybrid electric vehicles (HEVs) and even pure electric vehicles (EVs) [1–5]. However, the most popular mobile power, lithium-ion batteries (LIBs), which have achieved great success in a wide range of applications, are now limiting by its theoretical energy density. As a candidate, lithium-air batteries have received great attention due to its supreme theoretical capacity, in which, the cathode reactant oxygen can be acquired from ambient environment directly and the battery anode lithium metal has the

largest specific capacity relative to other metal materials (3842 mAh g⁻¹ vs. 815 mAh g⁻¹ for zinc and 2965 mAh g⁻¹ for aluminum) [6–10]. Both of them contribute to the highest specific energy density among the metal-based batteries. However, there are still many problems to be solved in the feasibility development of lithium-air batteries, such as high over potential, poor rate capability, terrible cycle ability and the specific energy density below theoretical value [11–14]. The solutions to all these problems depend on an effective cathode which can provide enough transfer channels for Li⁺ and O₂, accommodation for deposition and decomposition of insoluble discharge products, and catalytic activity for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [15].

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With abundant multidimensional nanoarchitectures and surface characteristics [16], carbon-based materials have shown great dynamism in cathodic studies. Graphene, a two-dimensional carbon nano-material with hexagonal honeycomb lattice composed of sp^2 hybrid orbitals by carbon atoms, has attracted a wide range of research interests since it was isolated firstly from the graphite by Novoselov and his co-workers in 2004 [17], due to its enormous surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$), outstanding thermal conductivity ($4840\text{--}5300 \text{ W m}^{-1} \text{ K}^{-1}$), high electrical conductivity ($\sim 2000 \text{ S cm}^{-1}$) and excellent mechanical properties [18,19]. However, the performance of the pure graphene cathode has been greatly limited by its perfect structure of defect-free [20–24]. Therefore, graphene is shaped into a wide variety of structures these years [25–27]. Creating porosity within the graphene structure and inducing curvature to bend the sp^2 hybrid structure can activate graphene for the desirable electrocatalytic activity [28]. Sun et al. reported a porous graphene cathode with different pore size architectures synthesized by a hard template method, which exhibited significantly higher discharge capacities than that of nonporous graphene [29]. Jie Xiao and his group prepared an unusual hierarchical arrangement of functionalized graphene sheet applying to Li–O₂ batteries. The unique bimodal porous structure provided a high density of reactive sites and microporous channels for rapid O₂ diffusion, thus an exceptionally high capacity [30]. Wang et al. synthesized a hierarchically porous carbon derived from graphene oxide (GO) gel by a facial and effective in situ sol-gel method, which displayed a high capacity and high-rate performance [31]. Such capability likewise derived from the porous structure that facilitates continuous oxygen flow in the O₂ electrode and provides enough void volume for discharge products accommodation. In addition, heteroatom doping can rearrange the charge distribution over material surfaces and thus introduce more reactive sites [32,33]. Since carbon atoms in the graphene hexagonal structure can be easily replaced by neighboring elements [28], various heteroatom-doped graphene cathodes have been commonly used in Li–O₂ batteries. A metal-free three-dimensional graphene material doped with nitrogen reported by Yang et al. delivered a high density of the ORR and OER active sites and facilitated the electrolyte and electron transports, applying to air cathode of metal-air batteries [34]. Zhi Yang and his co-workers compared sulfur-doped graphene with Pt/C modified electrodes as cathode catalyst, exhibiting better catalytic activity and great potential for a substitute for Pt-based catalysts [35]. Moreover, considering synergistic effects of the two heteroatoms, Lim et al. prepared nitrogen and sulfur dual-doped graphene nanosheets (NSGC) as cathodes for Li–O₂ batteries [36]. It can be seen that these modified cathodes showed substantially enhanced discharge capacity and improved rate capability, compared with pure graphene.

In this report, we developed a porous graphene foam to serve as battery cathode, which has a large number of defects by partially oxidizing the metal substrate during the chemical vapor deposition (CVD) process. The porous structure and abundant defects of the prepared graphene foam were analyzed by SEM and Raman scattering spectra. The battery with this cathode exhibited enhanced discharge capacity, high rate-capability, stable cycle ability, and so on.

Experimental

Synthesis of cathode material

In this study, the high-quality graphene foam was prepared via a conventional method of chemical vapor deposition (CVD). Commercial Ni foam was cleaned successively by isopropanol, acetone and deionized water with the assistance of ultrasonic sound [12]. The Ni foam substrates were then placed into a tube furnace and heated to different temperatures ($600\text{--}900\text{ }^\circ\text{C}$) with a gaseous environment of 15 vol% H₂ + Ar. Before graphene deposition, the Ni foam substrates were partially oxidized through the introduction of ambient air at given temperatures ($600\text{--}900\text{ }^\circ\text{C}$) for a limited time (30 s–300 s). After that, the oxidized substrates were continuously heated up to $900\text{ }^\circ\text{C}$ and kept at the temperature for 5 min with flowing gases of 20 sccm acetylene, 15 sccm hydrogen and 85 sccm argon. During graphene deposition, carbon atoms after pyrolysis will attach onto clean Ni surface to form graphene but not NiO_x surface, resulting in a high active graphene with abundant defects/holes. For some samples, the substrate of Ni foam was removed with a nitric acid solution in a volume ratio of 1: 1.

Physical characterizations

The morphology of different cathodes and discharge products were characterized by a field-emission scanning electron microscopy (SEM, Hitachi S-4700) and transmission electron microscope (TEM, JEOL2100F). A Rigaku X-ray diffractometer (XRD, D/max-Ultima IV) was used to analyze formation and decomposition of products before and after recharge. Raman scattering spectra (XperRam Compact, NanoBase, Korea) were obtained to research the introduced defects.

Electrochemical measurements

In order to test performance of the cathodes, Swagelok type cells [37,38] were used. The assemble process was carried out in a glove box (Braun, Germany) filled with high purity argon, in which H₂O and O₂ concentration are below than 0.5 ppm. A commercial lithium foil (Tansworld Enterprises LTD, China) was employed as anode and separated with cathode by a glass-fiber separator (Whatman GF/C, America). In addition, 40 μL organic electrolyte (1 M LiTFSI/TEGDME, Suzhou Chemical ReagentLTD, China) was instilled the system to fully wet it. Through the battery testing system (Neware, CT-3008), discharge-charge capacity, rate capability, cycle ability, voltage plateau and efficiency can be recorded and analyzed. We calculate the specific capacity based on whole cathode, i.e., graphene foam that is about 0.3 mg cm^{-2} .

Results and discussion

Morphology and structure

The SEM images of the as-prepared cathodes are shown in Fig. 1. Under low magnification in Fig. 1a, the foamed structure

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