A High Surface Area Carbon-coated 3D Nickel Nanomesh for Li-O₂ Battery

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Abstract: Nanostructured electrodes show great promises if used in battery and could improve the energy and power density of batteries. Herein, we propose to use a carbon-coated 3D Ni nanomesh as an air cathode for non-aqueous Li-Air (O₂) battery applications. In this study, we fabricate a 3 μm thick 3D Ni nanomesh, showing the excellent surface area to footprint area ratio (90 $\text{cm}^2/1 \text{ cm}^2$) and uniformly distributed pores on which we apply for the first time a conformal amorphous carbon coating. This carbon-coated 3D Ni nanomesh shows ~ 100 larger charge footprint capacity than that of the glassy carbon electrode. Thanks to its tunable properties, this nanostructured CNM could give the promises to achieve capacity higher than 6 mAh cm^{-2} for a CNM with the thickness of 100 μm , while the practical capacities of current air electrodes are in the range of 2 mAh cm^{-2} .

There has been considerable interest in non-aqueous Li-O₂ batteries in the past decade thanks to their high theoretical gravimetric energy density of 3505 Wh kg^{-1} , by far exceeding those of current lithium-ion batteries with lithium insertion host materials ($\sim 400 \text{ Wh kg}^{-1}$).¹ This large increase in gravimetric energy density comes from the fundamentally different reactions of the Li-O₂ battery chemistry, which relies on the reduction of gaseous oxygen to form solid lithium peroxide ($2\text{Li} + \text{O}_2 = \text{Li}_2\text{O}_2$, $E^0 = 2.96 \text{ V vs. Li}^+/\text{Li}$) or lithium oxide ($2\text{Li} + \text{O}_2 = \text{Li}_2\text{O}$, $E^0 = 2.91 \text{ V vs. Li}^+/\text{Li}$). However, the commercialization of Li-O₂ battery has not yet been considered since it suffers from several technical hurdles and the solutions have to be provided in respect to the selection of a stable electrolyte (such as ethers forming mainly Li_2O_2 during the discharge process),² and the optimization of the air cathode formulation and properties. Related to this last topic, the rechargeability of the lithium-oxygen battery is hindered by the formation of the insulator Li_2O_2 ,³ typically formed during discharge by reaction of Li^+ ions with O_2 radicals. The lithium peroxide accumulated in the pores of the cathode limits the practical

discharge performance of the battery. Moreover, it is difficult to decompose the lithium peroxide during the charge process unless high voltage ($> 4 \text{ V vs. Li}^+/\text{Li}$) is applied, which may bring additional parasitic reactions (e.g. electrolyte decomposition).

To date, research efforts have mainly focused on the development of porous cathode materials^{4,5}, and reaction catalysts^{6,7} introduced to increase the Li_2O_2 amount (and discharge capacity) and to enhance the Li_2O_2 plating and stripping kinetics. On the other hand, there have been insufficient amounts of reports concerning the design of 3D nanostructured binder-free electrode or current collector as an electrode template for application in metal-air batteries.^{7,8} Therefore, we believe it is of fundamental interest to clarify whether the direct increase in surface area, combined with nanoscale electrolyte compartment, could result in the enhanced volumetric power density per the same footprint unit area (cm^2). Thus our concept is to electrodeposit thin layers of Li_2O_2 on the large surface area of our 3D nanostructure electrode in order to reach large capacity (per footprint area) counting on the fact that decomposing thin layer of Li_2O_2 would be more effective than decomposing thick particles.

Recently, our group reported the fabrication of a 3D Anodized Aluminum Oxide (AAO) porous film uniformly grown on TiN/Si wafer by anodization of aluminum alloys.⁹ In that report, the mean pore size and the nanowire thickness could be systematically controlled by applying different anodization voltage and pH of the anodization bath. This AAO porous film could be converted into highly ordered 3D Ni nanomesh whose structure is determined by the primitive AAO template, followed by Ni plating and AAO etching. The brief schematic description of 3D Ni nanomesh fabrication process is shown in **Fig. 1a**. The 3D Nickel nanomesh is comprised of horizontally and vertically grown nanowires with the average thickness of 40 nm and the inter-wire distance of 60 nm, which are interconnected to each other, having approximately 90 times higher effective surface area (30 cm^2 per 1 μm thickness) per geometric footprint area (cm^2) with a possibility of being fabricated much thicker, depending on the initial thickness of aluminum alloys layer (**Fig. 1b**).¹⁰ Here, the 3 μm thick Ni nanomesh is equivalent to a 0.7 μm thick planar Ni according to

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Figure 1. The schematic view of 3D Ni nanomesh fabrication process on the Cu-doped Al/TiN/Si wafer and carbon coating process using CVD (a). The SEM images of pristine Ni nanomesh and nanowires are also shown (b).

Faraday's law with 76 % porosity. Despite these advantageous aspects, Ni itself could promote alternative conversion reaction¹¹ and detrimental side reactions such as electrolyte degradation, which disqualifies pure Ni as a binder-free electrode for Li-O₂ battery.⁸ Therefore, it is of great importance to find suitable material which could be deposited electrochemically or via other non-destructive deposition techniques such as chemical vapor deposition (CVD) for the 3D Ni nanomesh substrate.

Among various electrode material candidates, amorphous carbon was chosen as a coating material in this study because: i) the growth of glassy carbon via CVD could be performed at relatively low temperature (< 300 °C), preventing the 3D Ni nanomesh template from possible morphological deformation; ii) glassy carbon is one of the most well-known electrode materials, which is suitable to study the effects of coating and surface area enhancement during electrochemical cycling in Li-O₂ battery system. Therefore, the primary goal of this research is to show the feasibility of homogeneous material coating on 3D Ni nanomesh. The experimental CVD process is described in the experimental section of SI and allows us to obtain the carbon-coated 3D Ni nanomesh (CNM).

To check the homogeneity of carbon coating on the CNM, scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) were performed as

Figure 2. The scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) measured on carbon-coated Ni nanomesh.

illustrated in Fig. 2. The observed thickness of carbon layer on a single Ni nanowire from the CNM is 2 nm, which is homogeneously distributed over the nanowire as evidenced by EDS profile. On the other hand, it is important to shed a light on the conformality of carbon contents on Ni nanomesh from CVD process. Raman spectroscopy is one of the most sensitive techniques to investigate carbonaceous substances. To investigate the conformality of carbon-coating, three different points, the outer edge of deposition area (CNM-1), the inner edge of deposition area (CNM-2), and the center of deposition area (CNM-3), of a deposited template wafer piece (2x2 cm²) are selected and their corresponding Raman spectra are recorded as shown in Fig. 1S. The Raman spectra obtained on three different sites are identical, showing a G peak around 1600 cm⁻¹ and largely broadened D peak around 1350 cm⁻¹, which is commonly observable from amorphous carbon by virtue of the sp² hybridization disorder.¹²

In order to assess the electrochemical performances of our CNM in an O₂ environment, we selected an electrolyte stable in presence of O₂ radicals, favorizing the planar dissolution of Li₂O₂.^{13,14} Also, LiTFSi in DME is known to be one of the most stable electrolytes for Li-O₂ applications and form Li₂O₂ on the first discharge.¹⁵ To demonstrate the area enhancement effect, we selected two planar substrates: a Carbon-coated Ni planar (CNP) and a Glassy Carbon (GC) electrodes and evaluate their electrochemical behaviour under both O₂ and N₂ atmosphere for comparison purpose. Here, all samples are first measured under N₂ and then compared with those recorded under O₂. Fig. 3 illustrates the obtained CV curves of each sample (GC, CNP, and

Figure 3. The obtained cyclic voltammograms (CV) of commercial glassy carbon (black solid line), carbon-coated Ni planar (grey solid line), and carbon-coated Ni nanomesh (dashed line) measured under O_2 at a scan rate of 25 mV s^{-1} in the voltage range between 1.8 and 4.8 V using a modified glassy cell, which could clamp the wafer-type electrode. CV curves of glassy carbon and carbon-coated Ni planar substrate are shown separately at a different scale in the inset of the figure for clarity.

CNM) under O_2 atmosphere. The CV curves of the glassy carbon electrode show a distinctive reduction peak at 2.1 V. On the other hand, two oxidation peaks centered at 3.5 V and 4.0 V are recorded during oxidation process whose current density is majorly distributed in the voltage range between 3.0 and 4.0 V. The observed reduction and oxidation peaks are in good agreement with previously reported peaks from the plating and stripping of Li_2O_2 under relatively rapid scan rate.¹⁶ Meanwhile, the origin of broad current density increase from 4.3 V may be due to electrolyte degradation initiated by O_2 radicals.¹⁷ The calculated charge density of GC ($Q_{O_2-Q_{N_2}}$) is -6.04 mC cm^{-2} for reduction reaction and 1.56 mC cm^{-2} for oxidation reaction, respectively. To check the feasibility of carbon-coated Ni substrates, CV profiles of CNP are measured using the same experimental conditions applied on GC electrode under flow of N_2 and O_2 . The calculated charge density ($Q_{O_2-Q_{N_2}}$) for CNP is -1.62 mC cm^{-2} for reduction reaction, which is mainly attributable to the enhanced negative current density below 2.5 V. On the other hand, the relatively low current density of 0.18 mC cm^{-2} is obtained from the oxidation reaction with very broad current peaks centered at 3.5 V and 4.1 V. Even though the electrochemical activity of carbon-coated electrode fabricated via CVD process in this study is confirmed from a series of preliminary CV measurements, the calculated charge density of the planar CNP is lower than that of the GC. In such case, one of the most effective ways to improve the electrochemical kinetics and specific areal capacity of one electrode system is to enhance the electroactive surface area. To investigate direct surface area enhancement effects in terms of charge density under O_2 , the CV profiles of 3D CNM nanostructures are also recorded. The calculated charge density ($Q_{O_2-Q_{N_2}}$) for CNM is $-29.91 \text{ mC cm}^{-2}$ for reduction reaction and

Figure 4. The galvanostatic reduction and oxidation curves of glassy carbon, carbon-coated planar Ni, and carbon-coated Ni nanomesh with a reductive current rate of 0.1 mA cm^{-2} and an oxidative current rate of 0.05 mA cm^{-2} in the voltage range between 1.8 V and 4.0 V under flow of O_2 . The images obtained from HAADF-STEM for CNM after reduction (a) and oxidation (b) processes are demonstrated.

8.93 mC cm^{-2} for oxidation reaction, showing that the surface area enhancement could result in superior current density for both the reduction and oxidation processes even under relatively rapid CV scan rate. To further envisage the feasibility of the 3D nanomesh as a viable current collector, the galvanostatic reduction and oxidation measurements have been carried out on CNM and compared with those of GC and CNP in the voltage range between 1.8 and 4.0 V. This electrochemical potential window with 4 V cut-off was chosen as a maximum charging voltage since we expect the electrolyte to be stable below 4 V in the presence of O_2 . To minimize the irreversible capacity, the measurement is carried out with the reductive footprint current density of 0.1 mA cm^{-2} and the balanced oxidative footprint current density of 0.05 mA cm^{-2} . **Fig. 4** shows the galvanostatic reduction and oxidation profiles of each sample and their corresponding footprint capacities. As expected, we observed largely enhanced footprint capacity of $221 \mu\text{Ah cm}^{-2}$ from the reduction process and $193 \mu\text{Ah cm}^{-2}$ from the oxidation process with the faradaic efficiency of 87 %, whose values are 102 and 563 times higher than those of GC, respectively. To investigate the thicknesses of the electrodeposited Li_2O_2 after both galvanostatic reduction and oxidation, HAADF-STEM of CNM are recorded. Here, the

observed 10 nm thick layer (**Fig. 4a**) after the reduction process is reduced to 3 nm (**Fig. 4b**) after oxidation process, indicating that the Li_2O_2 plating and stripping bring no distinctive morphological deformation of 3D nanomesh framework. This result indicates that approximately 8 nm thick Li_2O_2 is deposited during the reduction process and 7 nm of this layer is stripped during the oxidation process, while 2 nm thick carbon layer is preserved, which could explain well the observed partial irreversibility (87.5 %). This observation is also in good agreement with previous report on the technical difficulty of stripping more than 5 nm thick Li_2O_2 layer.³ Nonetheless, the demonstrated plating and stripping of thin Li_2O_2 on and from CNM show that the 3D nanoarchitecture of the current collector and the nanoscale electrolyte compartment are beneficial for the enhancement of the footprint capacity and the reversibility for Li- O_2 battery.

In this study, we report the carbon coating on 3 μm thick 3D Ni nanomesh (CNM) via CVD and demonstrate its surface area enhancement effect in Li- O_2 battery for the first time. The obtained Raman spectra and EDS profiles show that the thin amorphous carbon layer is conformally distributed over the Ni nanowires with the thickness of 2 nm. The electrochemical activities obtained from CV and galvanostatic mode testing show that the specific current density and capacity of CNM are largely improved compared to those of glassy carbon (GC) and carbon-coated planar Ni (CNP). The greatly improved footprint capacity of CNM obtained in this study qualifies the 3D nanomesh as a promising electrode template for rechargeable battery technology when the volumetric capacity of the electrode material is a primary concern. For the next step, we suggest that the better utilization of nanosized electrolyte compartment for improved cyclic performance could be achieved by a combination of an optimized current density for plating thinner Li_2O_2 layer and the optimized battery components designs. Finally, 3D nanostructured electrode based on our CNM with even higher power density could be fabricated with thicker Ni nanomesh (> 100 μm) current collector, enabling specific footprint capacity higher than 6 mAh cm^{-2} . For large-scale energy storage application, the wafer-scale (> 200 mm) 3D nanomesh fabrication process needs to be further developed.

Keywords: Nanomaterial • Surface-area enhancement • Li- O_2 battery • Electrodeposition • Carbon-coating

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

This carbon-coated 3D Ni nanomesh shows excellent surface area to footprint area ratio ($90\text{ cm}^2/1\text{ cm}^2$) and ~ 100 larger charge footprint capacity than that of the glassy carbon electrode when used as an air cathode for non-aqueous Li-O₂ battery.

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