Carbon 136 (2018) 54–62

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Hierarchically porous carbon microspheres with fully open and interconnected super-macropores for air cathodes of Zn-Air batteries

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A R T I C L E I N F O

Article history:
Received 16 March 2018
Received in revised form
12 April 2018
Accepted 21 April 2018
Available online 23 April 2018

Keywords:
Hierarchically porous material
Carbon spheres
Interconnected super-macropores
Oxygen reduction reaction
Zinc-air battery

A B S T R A C T

Hierarchically porous materials have drawn extensive attention to construct effective air cathodes in newly developed zinc-air batteries. Here, we successfully fabricated hierarchically porous carbon microspheres (HCMs) with fully open and interconnected super-macropores by a strategy of high internal phase W/O/W double emulsions (HIPDEs). The as-prepared HCMs-supported platinum nanoparticles (Pt/HCMs) were employed as novel ORR catalysts for the air cathodes of Zn-air batteries. It was found that Pt/HCMs promised a nearly 100% Pt utilization and showed a higher current density and better durability than the commercial Pt/C on rotating disk electrode (RDE) setup and gas diffusion electrode (GDE)-based half-cell configurations, highlighting the importance of the fully open and interconnected super-macropores for improving the gas/liquid phases transport. Benefiting from the superior mass transfer, the Pt/HCMs-based Zn-air battery delivered high power density (190 mW cm^{-2}) and specific capacity (800 mA h g_{Zn}^{-1}) comparable to that of the commercial Pt/C-based battery. This study presents a new avenue to engineer catalyst to boost the performance of Zn-air batteries.

1. Introduction

Zn-air batteries (ZABs) have attracted much attention as a promising alternative technology to lithium-ion batteries because of their high theoretical energy density, safety, environmental benignity, and the earth-abundant zinc sources [1–4]. To date, ZABs has been successfully used in low power electronics, such as hearing aid devices, emergency power sources, and some portable products. Nevertheless, the power density of ZABs is still needed to be improved before more wide application. It is well known that the performance of ZABs is limited largely by the overall reaction rate of the oxygen reduction process at the air cathode [5–7]. Oxygen reduction reaction (ORR) is a sluggish tri-phase catalytic process, including gases (O_2), liquids (electrolyte), and solids (catalyst) [8]. It is crucial not only to synthesize highly active sites but to design a rational electrode structure to provide smooth mass transport for obtaining excellent ORR performance. The current state-of-the-art platinum supported on carbon catalyst is highly active for the reaction. The carbon support of commercial catalyst with an average pore diameter below 2 nm is easy to aggregate, resulting in an unsmooth mass transfer and breaking the tri-phase interfaces [9]. As a result, lower Pt utilization, oxygen starvation and water flooding often arise during operation [10–13], which seriously reduce the ORR performance and the power output of ZABs [1,14–16]. Therefore, the structure of electrode should be well designed and optimized for enhancing electrochemical performance.

In order to achieve efficient diffusion of the substances, hierarchically porous materials with well-defined pore dimensions are particularly interesting [17–19]. Ryoo and coworkers initiated to apply ordered mesoporous carbon materials as Pt support and excellent ORR performance had been obtained [20]. During the past decade, a series of meso-/microporous catalysts have been synthesized and applied to the air cathodes [21–23]. With respect to the liquid phase reactant/product in the reactions, macropores are more favorable than meso-/micropores since the physicochemical properties of the electrolyte in the macropores is similar to that in continuous body phase [24]. Therefore, many efforts have been made to fabricate hierarchically porous carbons with macro-/micro- [25], macro-/meso- [26,27], and macro-/meso-/micropores [28–30]. It has been proved that macropores can provide facile transfer and diffusion of reactants/products, and mesopores can afford sufficient spaces to highly dispersed active metals [31]. In

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https://doi.org/10.1016/j.carbon.2018.04.061

fact, the mass transfer property in porous materials is determined by not only the pores size but also their topologies, such as length, morphology and especially connectivity [9]. Only the interconnected pores which form a continuous phase within the porous medium, are effective for mass transport. While the non-interconnected and even the “dead-end” pores have little contribution to diffusion [32].

Interconnected macroporous carbon materials can be synthesized by hard templating method or emulsion templating [33–35]. Unfortunately, the majority of porous carbons prepared through these strategies are usually monolithic with long pore channels, which ultimately leads an increase in mass transfer resistances. From this point of view, small size hierarchically porous carbons with interconnected macropores are of great importance for ideal air cathodes [36,37]. Interconnected porous carbon spheres which could be synthesized by high internal phase W/O/W double emulsions (HIPDEs) integrate the advantages of carbon materials with spherical colloids, presenting excellent electron and mass transfer property for electrochemical catalysis [38]. So far, various polymer precursor double emulsions have been developed using micro-fluidic device, sedimentation strategy and catastrophic inversion method [33,39,40]. However, most of these methods were time-consuming and required special surfactants or equipment [41,42]. Herein, HIPDEs with fully open and interconnected 3D macroporosity have been fabricated by one-step emulsification, which is stabilized by span 80, a common small molecular surfactant. The derived hierarchically porous carbon microspheres (HCMs) are used as novel Pt support for ORR of Zn-air batteries (Scheme 1). The obtained HCMs exhibit hierarchical macro-/meso-/micropores, fully open and highly interconnected macroporosity networks, and smaller size compared with the monolith. Remarkable transport advantages have been achieved for the reactants and products in the ORR reactions. As a result, the HCMs-supported Pt catalysts achieve a nearly 100% Pt utilization and deliver a superior power-density ZABs (nearly 1.5 times) than that of the commercial Pt/C catalyst.

2. Experimental section

2.1. Materials

Styrene (St, Aladdin, 99%), divinylbenzene (DVB, Aladdin, 80%) were further purified by passing through a basic alumina column to remove the inhibitor before use. Sorbitan monooleate (Span 80, Tianjin Guangfu Fine Chemical Industry Research Institute), 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65, Energy Chemical Reagent), carbon tetrachloride (CCl_4, Aladdin, 99.5%), anhydrous aluminum chloride ($AlCl_3$, Aladdin, 99%), sulfuric acid (H_2SO_4, 98%, Beijing Chemical Co.) and sodium borohydride ($NaBH_4$, Macklin, 98%) were used as received. The deionized water was obtained from the Milli-Q System.

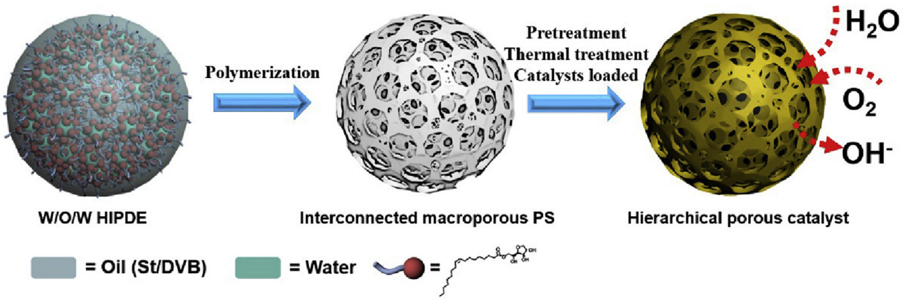
2.2. Synthesis of porous carbon spheres

Monodisperse polystyrene spheres (PS) were synthesized by in-situ polymerization of the HIPDEs. To prepare the emulsions, 0.5 ml surfactant Span 80 and 0.05 g V-65 initiator were dissolved in 2.25 ml mixture of St and DVB (1:1 vol). With the addition of 85% aqueous internal phase water, only 2 min of mechanical emulsification was performed on an ultratube disperser (IKA ultra turrax) under stirring speed of 6000 rpm. The resulted W/O/W latex was then poured into 30 ml water to dilute dense emulsion. After standing for 1 h, the upper emulsions were transferred to hot water with the temperature of 90 °C by dropwise for polymerization. After polymerization for 8 h, the obtained white flocculence were collected by filtration and then washed with ethanol repeatedly and then dried under vacuum at 60 °C. 1.0 g of as-prepared PS was dispersed in 30 mL of CCl_4 and swelled for 5 h at 75 °C, then 1.8 g of $AlCl_3$ was added to the above mixture. The reaction was carried out at 75 °C for 5 h under shaking. A solution of 6% HCl and acetone (1:1 vol) was added slowly to the resulting mixture. The product was filtered off and washed with ethanol and water several times and then dried at 60 °C. Before carbonization, the porous microspheres were pretreated by immersing in conc. H_2SO_4 at 120 °C for 5 h. Then, the sulfonated powder was washed repeatedly with deionized water until remaining H_2SO_4 was removed followed drying at 60 °C. The processes of cross-linking and acid treatment were employed to further increase polymerization degree and mechanical strength [43,44].

The sulfonated polymer spheres were firstly thermally treated at 600 °C. Then, the resulted carbon spheres were exposed to active gas at 850 °C to obtain HCMs. Thermal treatment was conducted in the tube furnace using a heating rate of 2.5 °C/min up to 350 °C, dwelling for 2 h, and heating resumed at a rate of 2.5/min up to 600 °C, dwelling for 2 h. The resulting carbon spheres were labeled as CS600. The activation of carbon spheres was performed in flowing nitrogen and heated from room temperature to 850 °C at a rate of 10 °C/min. After reaching the specified temperature, the gas mixture ($N_2/CO_2 = 1/1$) was introduced into the tube furnace for 4 h and then switched back to nitrogen to prevent further activation during the cool down process.

2.3. Pt catalysts synthesis

Sodium borohydride ($NaBH_4$) reduction method was employed to synthesize Pt/HCMs catalysts. Typically, 30 mg of HCMs were soaked in 3 ml of 2 mg/ml H_2PtCl_6 ethanolic solution with continuously shaking for 8 h, and then added $NaBH_4$ solution to have Pt ions reduced. The Pt/HCMs were obtained after filtrated, washed, and dried at 60 °C in vacuum overnight. To thoroughly investigate



Scheme 1. Schematic representation of the preparation process of Pt/HCMs.