Electrochimica Acta 147 (2014) 1–8

Contents lists available at ScienceDirect

Electrochimica Acta

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

A carbon powder-nanotube composite cathode for non-aqueous lithium-air batteries

P. Tan, W. Shyy, Z.H. Wei, L. An, T.S. Zhao *

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology Clear Water Bay, Kowloon, Hong Kong SAR, China

ARTICLE INFO

Article history:
Received 24 June 2014
Received in revised form 7 August 2014
Accepted 2 September 2014
Available online 22 September 2014

Keywords:
Lithium-air battery
Discharge capacity
Carbon powder
Cathode structure
Oxygen transport

ABSTRACT

Carbon powder has been predominately used to form cathode electrodes for non-aqueous lithium-air batteries, mainly due to their large specific surface area. An issue, however, with carbon-powder based cathodes is the large oxygen transport resistance due to limited pore spaces resulting from the packing with nanosized spherical particles, leading to a practical discharge capacity much lower than the theoretical value. The present work addresses this issue by proposing a *composite* cathode made of carbon powder and nanotubes for non-aqueous lithium-air batteries. The discharge performance characterizations show that the discharge capacity of the cathode with mixed carbon materials increases with an increase in the ratio of carbon nanotubes to powder. At the ratio of 1:1, the highest volumetric and the gravimetric capacity are achieved, which are respectively 67.2% and 36.3% higher than those with the cathode made of pure carbon powder. It is further demonstrated that the battery with the composite cathode at a fixed capacity of 1.0 mA h/cm^2 exhibits a cycle life of up to 50 cycles, which is nearly twice the cycle number of the battery with its cathode made of pure carbon powder. The mechanism leading to the improved performance can be mainly attributed to the improved oxygen transport as the result of enlarged pore spaces with an appropriate composition of spherical carbon powder and cylindrical carbon nanotubes.

1. Introduction

Since the emergence of a rechargeable lithium-air battery based on a non-aqueous polymeric electrolyte in 1996 [1], non-aqueous lithium-air batteries have attracted a great deal of attention due to the large theoretical capacity (3.86×10^3 mA h/g) and high voltage (2.96 V), which correspond to the energy density of 1.14×10^4 W h/kg. The capacity of non-aqueous lithium-air batteries is still two to four times higher than that of Li-ion batteries, even when taking into account of the entire battery system by volume [2]. This striking feature allows the lithium-air battery to be one of the most promising power sources for next-generation electric vehicles and portable devices [3].

However, before this technology can be viably commercialized, a variety of technical hurdles must first be overcome. The main challenges include the instability of electrolyte and electrode materials [4–7] caused by the active intermediates from the oxygen reduction reaction during discharge [8,9], the lower discharge capacity than the theoretical value, and the poor reversibility. In addition to these stated issues, a key factor that limits the capacity is related to the formation of Li_2O_2 during discharge [10,11], which is insoluble in the non-aqueous electrolyte and deposits in the void spaces of the porous cathode. The solid product continuously grows on the pore-solid surfaces with an increase in the discharge capacity [12], and ultimately blocks the respective pathways for the transport of oxygen and lithium ions. Due to the low electric conductivity of Li_2O_2 [13], the electron transport can also become resistant with the growth of the discharge product. As a result, the discharge process is terminated before the whole cathode volume is utilized, leading to an actual capacity much lower than the theoretical value.

Carbon powder materials, e.g. Super P and Ketjen black, have been predominately studied as the cathode electrode for non-aqueous lithium-air batteries, mainly due to the large specific

* Corresponding author. Tel.: +852 2358 8647
E-mail address: metzhao@ust.hk (T.S. Zhao).

http://dx.doi.org/10.1016/j.electacta.2014.09.074
0013-4686/

surface area. For example, Tran et al. [14] and Park et al. [15] investigated the discharge performance of activated carbon and various types of carbon powder, and found that micro-pores and some meso-pores could be blocked by the discharge product, suggesting that carbon powder with a high surface area associated with larger pores is needed. Hayashi et al. [16] found that the capacity was in proportion to the surface areas of the carbon powder, and the meso-pores seemed to function as active sites during discharge. Gao et al. [17] used various carbon powder materials to form the cathode, including Super P, Vulcan-XC72, Ketjen black and activated carbon, and showed that the carbon sources and loadings had a large impact on the discharge capacity. Zhang et al. [18] studied the effect of two types of carbon powder, Super P and Ketjen black, on the discharge performance; they also fabricated a novel composite cathode comprising these two types of carbon powder to increase the discharge capacity by 20%.

Previous studies suggest that for the cathodes made of carbon powder materials, although the specific surface area is large, small pores can be easily blocked by the solid product, causing a high oxygen transport resistance [18]. As a result, the utilization of the void volume in the cathode is low, leading to a discharge capacity much lower than the theoretical value. To address this issue, in this work we propose to form a *composite* cathode of non-aqueous lithium-air batteries with a mixture of carbon powder and nanotubes. The morphology of the cathodes made of carbon powder and nanotubes at different weight ratios before and after discharge was examined, and the product chemical composition was also detected. The rate and cycle performance of the battery with the *composite* cathode were tested, and compared with the battery with the cathode made of pure carbon powder. The correlation between the discharge capacity, the pore spaces, and the transport resistance of oxygen was studied.

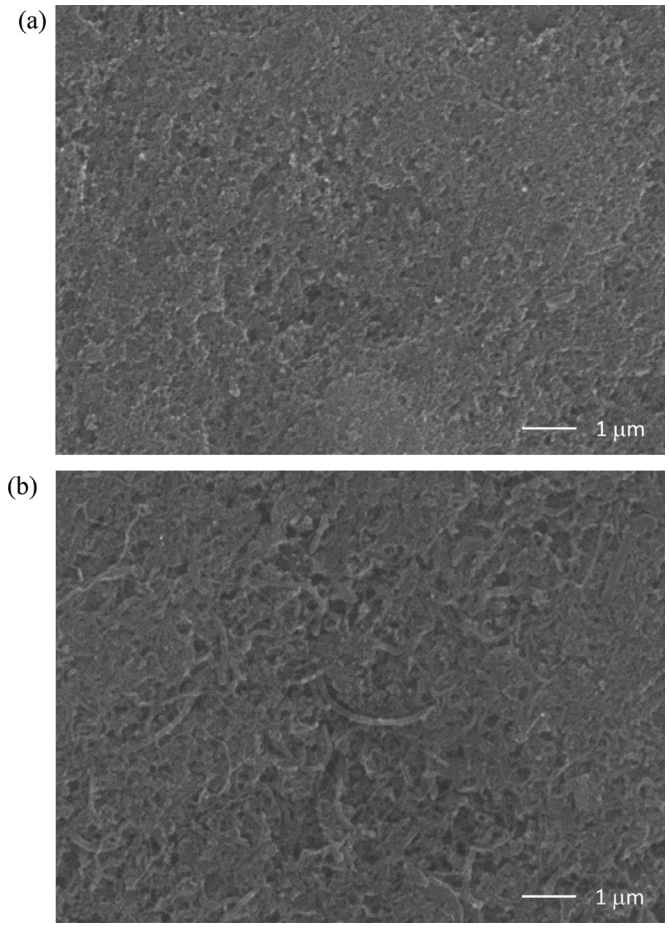

Fig. 1. Morphology of the cathode before discharge (10000×) made of (a) pure carbon powder, (b) mixed carbon powder and nanotubes.

2. Experimental

2.1. Cathode fabrication

The carbon powder applied in this work is Ketjen black EC-600JD with a diameter of approximately 20 nm (AkzoNobel Co. Ltd., China). The carbon nanotubes are multi-walled with diameters ranging from 40 to 60 nm and lengths ranging from 5 to 15 μm (Shenzhen Nanotech Co. Ltd., China). The specific surface area and pore size distribution of carbon powder and nanotubes were analyzed by liquid nitrogen sorption measurements based on the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

The carbon nanotubes were added to the carbon powder with different weight ratios, and mixed with polytetrafluorethylene (PTFE) as the binder at the dry weight ratio of 7:3. Ethanol was added as a dispersing agent and then the slurry was ultrasonically stirred for 1 hour. After being air-dried, the mixture was rolled to the thickness of 350 μm and cut into the film electrode with the diameter of 10 mm. The carbon loading of the cathode electrode ranged from 7.5 to 11.5 mg. Finally, all the electrodes were baked at 240 °C and sintered at 350 °C, both for 1 hour.

2.2. Battery assembling and test

The lithium-air battery contains a lithium metal foil as the anode, a glass-fiber separator (Whatman GF/C), and the carbon cathode as prepared. 200 μL 0.25 M lithium perchlorate ($LiClO_4$, Sigma-Aldrich, 98%) in tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich, 99%) was added in the battery to fully saturate the separator and the cathode. The entire battery

Table 1
Geometrical properties of the two carbon materials

Carbon material	Surface area, m^2/g	Micropore surface area, m^2/g	Mesopore surface area, m^2/g	Macropore surface area, m^2/g	Total pore volume, cm^3/g	Mesopore volume, cm^3/g	Macropore volume, cm^3/g
Carbon nanotubes	48.92	0.01	27.17	21.74	0.16	0.08	0.08
Carbon powder	1334.40	12.10	648.55	673.75	2.30	1.32	0.98