Experimental Study on Preparation of Ag Nanoparticles Doped Fullerenol for Lithium Ion Battery Application

*Fang Fang Wang, Chen Wang, Rui Qing Liu, Dong Tian, Ning Li**

Department of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China

The XPS constituent analysis of the pyrolysis product of $Ag_4C_{60}O_9(OH)_{12}$ at the temperature of 250°C, yielded the following atom concentrations: %C=77.89, %O=16.69, %Ag=5.51. Four Ag metal atoms per fullerenol molecule for a molecular formula of $4Ag/C_{60}O_9(OH)_4$ was given out, based on the pyrolysis mechanism from TGA results. And Ag exists in the state of single metal, not ion. The XPS constituent analysis of the pyrolysis product of $Ag_4C_{60}O_9(OH)_{12}$ at the temperature of 300°C, yielded the following atom concentrations: %C=81.07, %O=13.27, %Ag=5.66. And its molecular formula is $4Ag/C_{60}O_{10}$, Ag exists in the state of single metal. In the same way, constituents of the pyrolysis product of $Ag_4C_{60}O_9(OH)_{12}$ at the temperature of 350°C were analyzed using XPS. And the obtained atomic concentrations for C(81.07%), O(10.32%), Ag(5.36%), indicate four Ag metal atoms per fullerenol molecule for a molecular formula of $4Ag/C_{60}O_7$. In addition, constituents of the pyrolysis product of $Ag_4C_{60}O_9(OH)_{12}$ at 150°C is written as $4Ag(metal)/C_{60}O_5(OH)_{12}$ on the basis of pyrolysis mechanism in Eq(3).

Table 1S Pyrolysis products of $Ag_4C_{60}O_9(OH)_{12}$ treated in Argon atmosphere at different temperatures.

Pyrolysis temperature	Constituent	Molecular Formula of fullerenol in mixture
150°C	$4Ag(metal)/C_{60}O_5(OH)_{12}$	$C_{60}O_5(OH)_{12}$
250°C	$4Ag(metal)/C_{60}O_9(OH)_4$	$C_{60}O_9(OH)_4$
300°C	$4Ag(metal)/C_{60}O_{10}$	$C_{60}O_{10}$
350°C	$4Ag(metal)/C_{60}O_7$	$C_{60}O_7$
400°C	Ag exists in the state of single metal; And fullerene nucleus decomposes.	

Preparation of Samples:

Coin cells were treated at different potentials using a galvanostatically charge-discharge test system. After removing from the testing system, the coin cells were disassembled in a glovebox under the protection of argon. Finally, the material on surface of electrode was collected, and used for further XPS measurements. Samples were then obtained in accordance with the method as described above.

Table 2S Test parameters for electrode polarization

Sample	Test parameters							Actual Voltage
	STs	D,E	STs	C,E	STs	D,E	STs	
Fullerenol 2	5min	0.1mA 0.04V	5min	0.1mA 2.0V	5min	0.1mA 0.10V	2hours	0.37V
Fullerenol 3	5min	0.1mA 0.04V	5min	0.1mA 1.0V	2hours	—	—	0.82V
Fullerenol 4	5min	0.1mA 0.04V	5min	0.1mA 1.6V	2 hours	—	—	1.35V

ABBREVIATIONS: Standing time (STs); Discharging current and ending voltage(D,E); Charging Current and ending voltage(C,E)

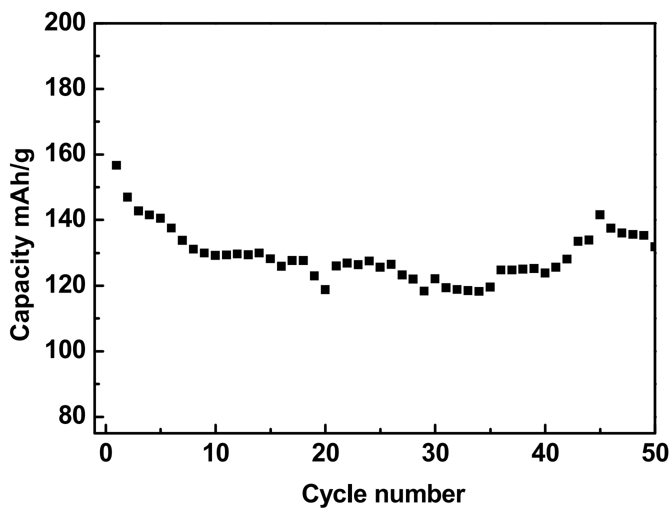


Figure 1S Cycling performance of acetylene black

As shown in Figure2S, the fitted peaks with a binding energy at 284.8ev has been assigned to non-oxygenated carbon, the peak at 286.3eV to mon-oxygenated carbon (-C-O-bands formed after dehydration), the peak at 288.9eV to hemiketal carbon, and the peak at 290.1eV to carbonyl carbon. These four peaks remain unchanged in the electrode sample treated with reduction potential of 0.4V, which indicates no changes in chemical speciation of carbon. The XPS for $Ag_{3d5/2}$ remains unchanged after charge

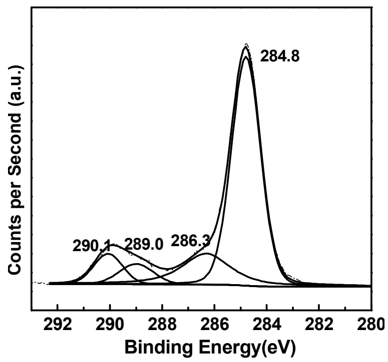
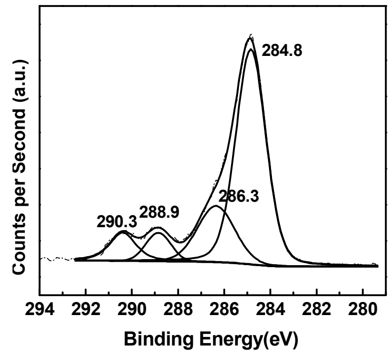
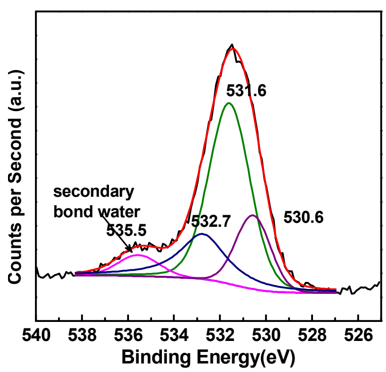
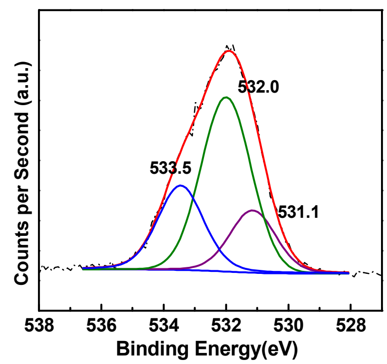
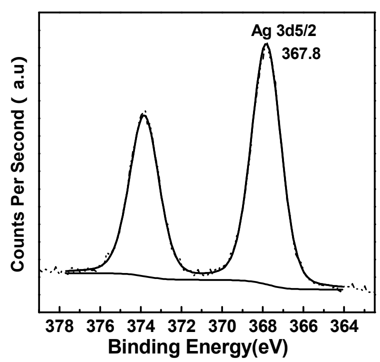
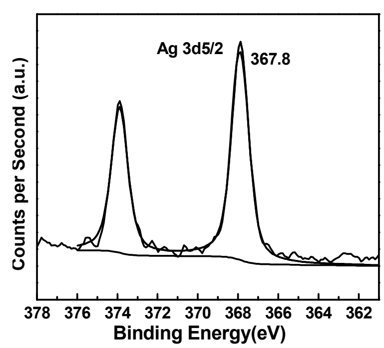
	(a)$Ag_4C_{60}O_9(OH)_{12}$	(b)$Ag_4C_{60}O_9(OH)_{12}$treated with reduction potential of 0.4V
C_{1s}		
O_{1s}		
$Ag_{3d5/2}$		

Figure2S XPS spectrum of C1s, O1s, and Ag 3d5/2 binding energy and the curve-fitting analysis results of anode materials: (a) $Ag_4C_{60}O_9(OH)_{12}$; (b) $Ag_4C_{60}O_9(OH)_{12}$ electrode treated with 0.4V reduction potential.

process. In contrast, the fitted peaks of O1s changed a lot after treatment with reduction potential of 0.4V. The fitted peak with a binding energy at 532.7eV is assigned to carboxyl oxygen(C=O), the peak at 531.6eV to hydroxide oxygen(–O-H), and the peak at 530.6eV to alkoxide oxygen(–OAg). These three peaks shifted to

533.5eV, 532.0eV and 531.1eV in the $Ag_4C_{60}O_9(OH)_{12}$ electrode sample treated with reduction potential of 0.4V, which shows a significant change in chemical speciation of oxygen atoms on the molecule. Therefore, $Ag_4C_{60}O_9(OH)_{12}$ as anode material for lithium ion batteries may have a different charge/discharge mechanism, compared with Ag NPs doped fullerenol ($Ag/C_{60}O_{10}$). It seems that the oxygen atoms of $Ag_4C_{60}O_9(OH)_{12}$ have great impacts on the performance of lithium ion batteries.

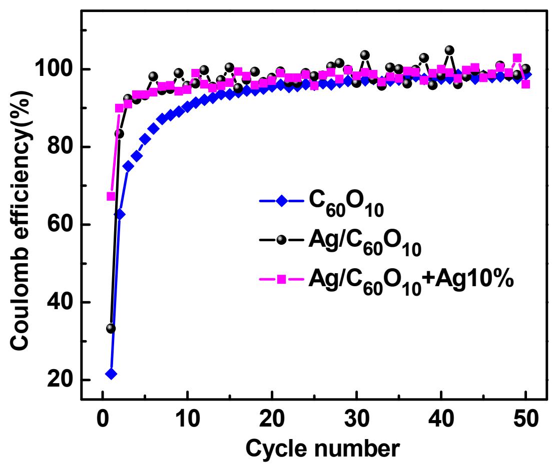


Figure 3S Cycle performance of $C_{60}O_{10}$, $Ag/C_{60}O_{10}$, and $Ag/C_{60}O_{10}$+Ag10%