Journal of Industrial and Engineering Chemistry 18 (2012) 726–730

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Effects of the structural characteristics of carbon cathode on the initial voltage delay in $Li/SOCl_2$ battery

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A R T I C L E I N F O

Article history:
Received 31 May 2011
Accepted 16 July 2011
Available online 24 December 2011

Keywords:
$Li/SOCl_2$ battery
Initial voltage delay
Carbon cathode
TMV

A B S T R A C T

The study investigates electrochemical behaviors of $Li/SOCl_2$ batteries based on structural features of carbon cathodes to find out solutions of initial voltage delay, a natural problem of the batteries. The structural features of the carbon cathodes in the $Li/SOCl_2$ batteries are directly related to the transient minimum voltage (TMV) and the initial voltage delay, the inevitable fault in the batteries, and the study confirms possibilities to solve inherent problems of the batteries by structurally adjusting carbon cathodes. Low density of carbon cathodes inhibits the TMV increase, the initial voltage delay more than high density. The operating voltage of the battery may rise with increasing electronic conductivity of the carbon cathode, however, it fails to improve the TMV and the delay. The study shows that expanding carbon cathode volume shrinks a gap between the lithium and the carbon cathode, pressurizing and destroying passivation films, and improving the TMV and the initial voltage delay. Based on this, it is expected to manufacture excellent Li/SO_2Cl_2 batteries by improving the initial voltage delay as adjusting aging lapse and pressed density.

1. Introduction

The $Li/SOCl_2$ battery has 3.6 V of high nominal voltage and 380 Wh/kg of energy density, therefore, it is a very suitable lithium primary battery for power sources of electronic devices requiring high output and capacity. The high output and capacity of the $Li/SOCl_2$ is attributed to structural features composed of cathode with carbon plates not directly involved in the electrode reaction, as well as using metal lithium as an active material and anode and $SOCl_2$ as an active substance for cathode and $LiAlCl_4$ as dissociated electrolyte [1–3]. Because the freezing point of $SOCl_2$ is lower than −110 °C, the electrolyte solution does not freeze under cryogenic condition, which makes it possible to operate $Li/SOCl_2$ batteries under any cryogenic conditions. Also, this forms passivation films of LiCl on lithium surface as a result of electrode reaction written in (1), giving less than 1% of magnetic discharge rate per year.

$$4Li_{(s)} + 2SOCl_{2(l)} \rightarrow 4LiCl_{(s)} + S_{(s)} + SO_{2(g)} \qquad (1)$$

However, the advantage of creating passivation film in the $Li/SOCl_2$ battery becomes the cause of temporary halting battery operation by dropping the operating voltage to a very low level called the 'transition minimum voltage (TMV)'. The phenomenon called the 'initial voltage delay' is recovered after a certain period of time but it causes serious problems like operation failure for batteries stored for a long time [4,5]. Therefore, the initial voltage delay is called an inherent problem in the $Li/SOCl_2$ battery, however, there have been many researches to solve or relieve this issue [5–9]. Previous researches aimed at improving the initial voltage delay consist of two categories. The first is to inhibit passivation films from growing by applying polymer materials on the lithium surface [5] and the second is to improve films by interfering with growing passivation films using electrode additives [6–8]. The concept of previous researches is to block or reform passivation film growth, the cause of the initial voltage delay, however, the problems in the delay have not been effectively solved out.

Here, the study has sought methods to remove the initial voltage delay by easily and quickly destroying the passivation films form on the lithium anode surface when applying loads to the battery while maintaining the advantage of the films which inhibits magnetic discharge of the battery. Polarization between the film and electrode solution is utilized to break the passivation films. The polarization generated in the battery after loads are connected may be settled in case that the reduction reaction starts in the initial carbon cathode. That is, ions in the solution start to move to reduce the surface polarization in case that the

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doi:10.1016/j.jiec.2011.11.118

polarization moves to the carbon surface after taking the reduction reaction in the carbon cathode. Then, the oxidation reaction in the lithium is stimulated to get rid of the polarization in the electrolyte. The settlement of polarization in the battery is commenced in the reduction reaction of the initial carbon cathode, creating force to break the passivation films. To accelerate breaking speed of the films, the speed of reducing battery polarization shall be improved and the internal resistance of the battery shall be minimized to achieve higher reduction speed. The internal resistance of the battery consists of carbon cathode resistance, lithium anode resistance and electrolyte resistance, and the study seeks to investigate forces to break the passivation films from carbon cathodes. The carbon cathode shall have excellent electron conductivity and ion movement, and minimize resistance due to the reduction reaction to minimize the carbon electrode resistance. This feature depends on the structural properties of the carbon cathode.

Therefore, the study seeks to find out solutions to initial voltage delay through improving breaking speed of passivation films due to changes of structural properties in the carbon cathode. To this end, the study investigates electrochemical features of the battery including the TMV and the initial voltage delay time due to spherical and cylindrical particle features with difference formation of the carbon black, carbon material for the cathode, density of the pressed cathode, improving electron conductivity adding Ni powder to the carbon cathode and expansion of the carbon cathode from penetrating electrolyte.

2. Experimental

2.1. Materials

The lithium anode for the battery is used by extruding lithium ingot (99.99%) to foil and micro glass fiber is used for separator. 1.0 M $LiAlCl_4/SOCl_2$ is used for the electrolyte by injecting and reacting $AlCl_3$ (Aldrich, 99.99%) and LiCl (Aldrich, 99.99%) with $SOCl_2$ (Lenxess, 99.99%). The carbon material for the carbon cathode is carbon black with the weight ratio of 7 and 3 for acetylene black (Denka black 50% compressed) and ketjen black (EC-300J), respectively. Polytetrafluoroethylene (PTFE) and isoprophyl achohol (IPA) are sprayed to the carbon black with adhesive binder to form the electrode and kept wet. The wet carbon black have a spherical form by granular mixing through the mixer with no gravitation and the shape changes to a cylinder through secondary process with granule pelletizer by increasing IPA content in the carbon black. After treating natural dry (55 °C, 2 h) and forced dry (150 °C, 2 h), the composition is stored in a dry room with less than 5% of relative humidity to use it for the carbon cathode.

2.2. Methods

2.2.1. Manufacturing batteries for test

The carbon cathode is pressed to form cylindrical type by putting granular carbon black composition in the dry room into the cylindrical mold with 10 mm diameter and 14 mm height. Then, the carbon cathode is prepared to have compact density between $0.3\ g/cm^3$ and $0.4\ g/cm^3$ by adjusting pressing pressure for the cylindrical compact. Also, the carbon cathode is prepared by adding 1 wt% of Ni powder (Aldrich, less than 325 mesh) while manufacturing carbon black composition with spherical granule to investigate correlation between the TMV and the initial voltage delay depending on electron conductivity of the carbon cathode. Also, the volume expansion of the carbon cathode is proportial to the moisture content of the electrolyte and prepared depending on the aging time right after injecting the electrolyte into the battery which uses the carbon cathode with $0.3\ g/cm^3$ of the pressed density.

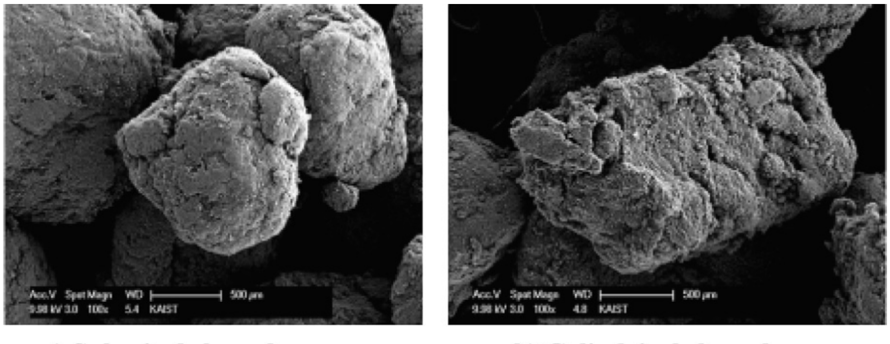
2.2.2. Performance test and analysis

The test battery is manufactured with 1/2AA size of Bobbin type by using the carbon cathode prepared based on the method above to perform electrochemical analysis. The electrochemical properties are measured by pulses, the difference between the TMV and the initial voltage delay and discharge capacity and compared by measuring the impedance depending on volume expansion of the carbon cathode with aging time using EG&G 273A and SI 1255.

3. Results and discussion

3.1. Feature of carbon black granule for the carbon cathode

The filling density of the carbon black composition manufactured with spherical or cylindrical types to manufacture the carbon cathode and the real density of carbon cathode formation using the composition are measured. The filling density is $0.166\ g/cm^3$ for spherical granule and $0.126\ g/cm^3$ for cylindrical granule and the real density of manufactured carbon cathode formation is $0.40\ g/cm^3$ for spherical and $0.30\ g/cm^3$ for cylindrical granules, showing that the cylindrical type has lower filling density than that of sphere, as well as formation density for the cathode. This result may be confirmed through analysis result of electro-microscope because the formed carbon black has higher geometric uniformity for spherical types than cylindrical type, as well as good packing structure. Fig. 1 is a picture of carbon black composition with spherical and cylindrical types taken by the electro-microscope. As shown in the picture, the formed carbon black composition has sizes between 800 and 1400 μm, indicating that the cylindrical type has less uniformity.



a) Spherical shaped **b) Cylindrical shaped**

Fig. 1. SEM photograph for shape of carbon blacks and the surface of carbon electrode prepared by using these granulated carbon blacks.