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The effect of lithium loadings on anode to the voltage drop during charge and discharge of Li-ion capacitors

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HIGHLIGHTS

- Investigated the voltage drop from Li-ion capacitors during charge and discharge.
- Demonstrated the importance of loadings of the stabilized lithium metal powders in Li-ion capacitors.
- Discussed mechanisms for causing the voltage drop of Li-ion capacitors.

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ABSTRACT

The IR voltage drop from the anode and cathode of Li-ion capacitors during charge and discharge was studied. Li-ion capacitors were made with activated carbon cathode and hard carbon anode with different loadings of stabilized lithium metal powder (SLMP). It was found that the LICs with high SLMP loadings showed smaller voltage drop than LICs with low SLMP loadings. It was also found that at low SLMP loadings, the IR voltage drops at high cell voltages were smaller than that at low cell voltages; while at high SLMP loadings, small IR voltage drops were obtained for both low and high cell voltages. The electrochemical impedance spectroscopy confirmed that voltage drops are directly related to the internal resistances of Li-ion capacitors.

1. Introduction

Pursuing more efficient energy storage devices which can provide high energy density, good power performance and long cycle life is always a popular research topic all over the world. The conventional electrochemical double-layer capacitors (EDLCs), which contain two symmetrical activated carbon electrodes with high surface area and porous structure, have the characteristics of high power and long cycle life; However, the energy density of the EDLCs is less than 10% of that of a lithium (Li)-ion batteries (LIBs), which restricts its application in many fields including hybrid electric vehicles (HEVs), electric vehicles (EVs) and other large-scale energy storage systems. Therefore, in recent years considerable research has been focused on the development of higher energy density supercapacitors. Among all the energy storage systems that have been investigated and developed in the last years, Li-ion Capacitors (LICs) have emerged to be one of the most promising because LICs can achieve higher energy density than conventional EDLCs, and better power performance than LIBs as well being capable of long cycle life. LICs contain a pre-lithiated LIB anode electrode and an

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EDLC cathode electrode [1–3].

Extensive research has been done to optimize the electrochemical performance of the LICs [4–21]. Recently, Puthusseri et al. [22] improved the energy density of LICs using polymer-derived porous carbons as cathode; Ren et al. [23] utilized pre-lithiated graphene nanosheets as negative electrode materials to achieve high power and energy density LICs; Schroeder et al. [24] compared the soft carbon and graphite anode material in the electrochemical performance in LICs, and found that soft carbon represented a promising alternative to graphite especially in the high rates applications. In the LICs energy storage system, anode pre-lithiation is a key process for assembling the LICs. Fuji Co. [6] proposed that a third electrode of Li metal can be used for pre-lithiation of the graphite electrodes as shown in Fig. 1. The first company to utilize a third electrode of Li metal to pre-lithiate the anode and produce LICs was JM Energy and the energy density of their LICs reached approximately 10 Wh/kg with a very stable cycle life.

Stabilized Li metal powder (SLMP®) is a pioneering and revolutionary material and technology developed by FMC that is able to provide electrochemically energy carrier as rechargeable Li atom for all types of Li based energy devices. SLMP is comprised of spherical particles with controlled particle size and surface area. SLMP is made by agitating a mixture of molten Li metal in a hydrocarbon oil at dispersion speeds [25,26]. The thickness and chemistry of the protective coating layer can be tailored and engineered based on user preference. SLMP can offer a capacity as high as 3600 mAh/g [27] and still can be safely introduced to the energy storage devices in a dry room atmosphere. Extensive studies have been done using SLMP in Li-ion battery energy storage systems [27–30]. Previously, we have reported a LIC with activated carbon (AC) cathode and hard carbon (HC)/SLMP anode electrodes with high energy density, high power density and long cycle life [31–34,47,48]. Instead of using a third Li foil electrode to pre-lithiate the anode, our group was the first to propose a pre-lithiation process by method of pressing SLMP on the surface of hard carbon anode electrodes in the LICs energy storage systems as displayed in Fig. 2. After the SLMP was applied onto the surface of the hard carbon anode electrodes, Li from the SLMP intercalated into the hard carbon when the electrolyte was filled into the cell. SLMP provides electrochemically active Li source as the energy carrier for capacitor. This high energy density concept of the LIC with such a novel structure as a conventional two-electrode rather than three-electrode cell has already been demonstrated in the laboratory using both coin cells and pouch cells [31–34,47,48]. As such, the usage of expensive copper mesh used to attach Li metal foil in three-electrode configuration as developed by Fuji Co. [6] is avoided.

Compared to the EDLCs having applied aqueous electrolytes with high conductivity, the LICs using nonaqueous electrolytes have serious problems with high power performance because of the overpotential on the high rate charge–discharge process. Usually, an Ohmic drop due to the electronic or ionic current flow, and a decrease in the voltage that is used for driving the reactions and the concentration gradients in a test cell [20] result in the IR drop in LICs. Despite numerous papers that have been published on the LICs, very few reports have discussed the effects of anode SLMP loadings on the IR drop of LICs in detail.

A useful tool in evaluating the effectiveness of the SLMP loading is electrochemical impedance spectroscopy (EIS), a process by

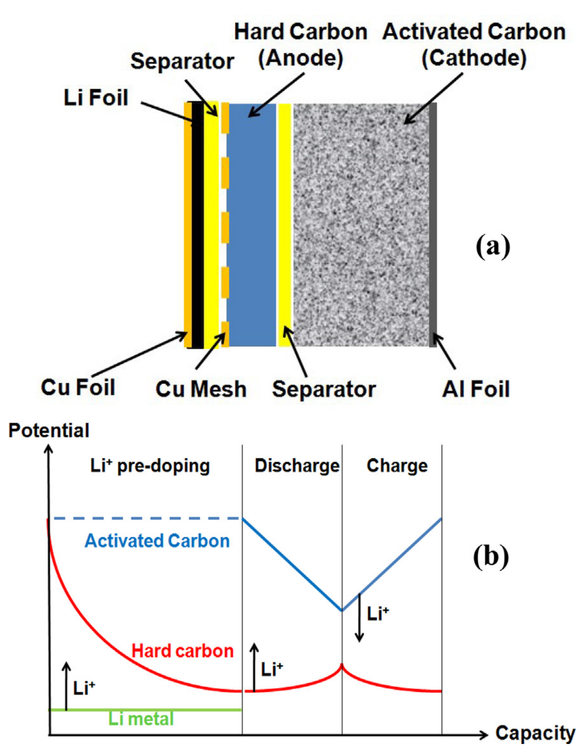

Fig. 1. (a) A schematic diagram of a three-electrodes (Li foil as the third electrode) Li-ion capacitor configuration and (b) the charge transfer between three electrodes during initial charge and discharge cycling.

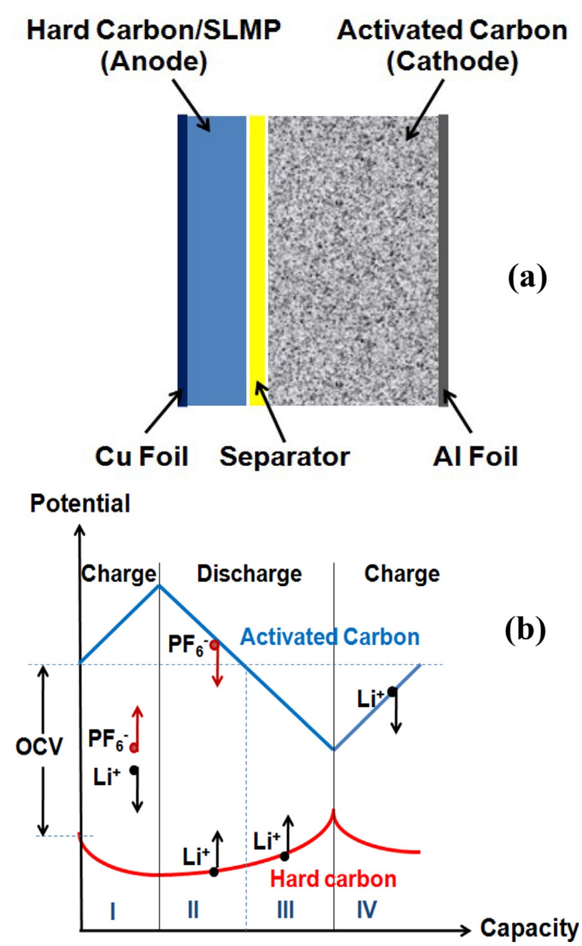

Fig. 2. (a) A schematic diagram of the AC/HC-SLMP novel two-electrodes Li-ion capacitor configuration and (b) schematic ion transfer in the Li-ion capacitor when the cell voltage greater (I and II) and lower (III and IV) than OCV.