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Short communication

Electrical analysis of Li/$SOCl_2$ cell connected with electrochemical capacitor

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Abstract

A Li/$SOCl_2$ bobbin-type cell, connected in parallel with an electrochemical capacitor, is investigated in order to overcome the voltage delay problem at high-rate discharge. In spite of the high internal resistance of the Li/$SOCl_2$ cell due to the passivation, the voltage delay is suppressed. Impedance measurements, in which the cell is separated from the capacitor, explain the suppression process clearly. The electrochemical capacitor operates as a high-current buffer and voltage-delay suppressor for the Li/$SOCl_2$ bobbin-type cell.

Keywords: Voltage delay; Parallel connection; Electrochemical capacitor; Impedance; Lithium battery

1. Introduction

A Li/$SOCl_2$ cell is an attractive primary battery with high specific energy, long shelf life, and a relatively long operating life [1]. Practical uses for this cell is as power sources in applications that require long operating life such as automatic meter reading (AMR) systems, global positioning system (GPS) tracking devices, RFID transponders, and security devices. Typically, the electrical consumption of such systems includes a sustained low background current of several microamperes and intermittent current pulses with amplitudes of several tens to several hundreds of milliamperes and a duration of milliseconds.

Unfortunately, during storage under open-circuit conditions or under low background currents the lithium anode of the Li/$SOCl_2$ battery is passivated by a film that substantially reduces the operating voltage of the battery [2–4]. As a result, during high current pulses, the cell voltage drops to a low level. This voltage-drop problem can be partially overcome by adding an organic compound such as polyvinyl chloride [5], or an inorganic compound such as SO_3, to the cell solution [6] for modifying the passive film to increase its conductivity. Such additives do not, however, completely solve the passivation problem. Another possible approach is to increase the surface area of the cell electrode. For example, the low surface-area of the bobbin-type design can be replaced with a 'jelly-roll' version that has a high electrode surface-area [1]. Unfortunately, this provides only a partial solution to the problem since, after 1–2 years of operations, jelly-roll cells also suffer passivation and low-voltage problems. Another disadvantage of the jelly-roll design is that cells may explode under certain conditions such as short-circuits, compression or nail penetration [7].

Recently, connection of the battery in parallel with an electrochemical capacitor has been suggested to be beneficial for high-current pulse applications [9]. There are, however, very few reported investigations of the electrical characteristics of the system in detail. Accordingly, this paper examines the electrical characteristics of a Li/$SOCl_2$ bobbin-type cell connected to a capacitor. Particular attention is paid to using the capacitor as means to suppress the voltage delay due to the passivation.

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2. Experimental

2.1. Preparation of test cells

The Li/$SOCl_2$ cell used in these experiments was the SBD02 unit manufactured by Vitzrocell Co. Ltd. The SBD02 is a D-size cell with a ‘bobbin’ carbon cathode configuration. This cell was designed for low-rate (<10 mA) applications and good safety by limiting the apparent electrode surface-area. The nominal capacity of the cell is 19 Ah at a discharge rate of 4 mA at 25 °C. The basic materials and construction of the cell have been described elsewhere [8]. In order to suppress the voltage delay, Li/$SOCl_2$ cells were connected in parallel with electrochemical capacitors, type EDLC, *PowerStor*®, of capacitance of 0.22, 0.47, and 0.68 F. Before connection, the EDLCs were fully charged to 3.65 V, which is the open-circuit voltage of the Li/$SOCl_2$ cell. After the parallel connection, the voltages of the Li/$SOCl_2$ cell and the EDLC were finely fluctuated and then stabilized after several hours. All these ‘hybrid cells’ were stored for 1 day at room temperature before undergoing electrochemical experiments.

2.2. Electroanalytical tests

Electrochemical measurements were preformed to evaluate the electrical characteristics of Li/$SOCl_2$ and hybrid cells. The voltage variation was measured during constant current discharge at 500 mA, which is too high a rate for the Li/$SOCl_2$ bobbin-type cell. The impedance of the hybrid cell was measured in order to clarify the suppression effect of the voltage delay. All measurements were performed by Im6e (Zahner-elektrik GmbH & Co., KG) and were carried out at room temperature. The resulting data were compared with those for a Li/$SOCl_2$ bobbin-type cell under the same conditions. Before the experiments, it was first necessary to clarify the characteristics of the EDLCs. In particular, the potential window of the EDLC was investigated in order to evaluate the benefits of making a parallel connection with the Li/$SOCl_2$ cell.

3. Results and discussion

3.1. Characteristics of EDLC for hybrid cell

Cyclic voltammetric (CV) curves for 0.22, 0.47, and 0.68 F EDLCs are compared in Fig. 1. All CV curves show near rectangular shape without any peaks that indicates that charging and discharging takes place at a constant rate over the voltage range of 0.0–5.0 V, which is generally indicative of a capacitative nature [9,10]. The measured currents naturally increase with the capacitance of EDLCs. Given these results, the EDLCs are very reasonable for the hybrid cell because the Li/$SOCl_2$ cell is used in the voltage range of 2.0–3.67 V.

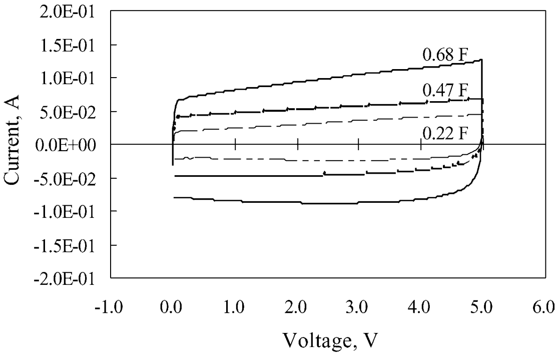

Fig. 1. Cyclic voltammograms of: 0.22, 0.47 and 0.68 F EDLCs; scan rate: 100 mV s^{-1}; voltage range: 0.0–5.0 V.

The ac impedance spectra of the EDLCs are given in Fig. 2(a). The spectra appear as a single semicircle in the middle-frequency range (1.5 kHz to 100 Hz) together with a line inclined vertically to the real axis in the low-frequency range (100–1 Hz). At 1.5 kHz, the intercept with the real-axis signifies the bulk resistance of the electrolyte. The semicircle represents the resistance and the capacitance of the porous carbon electrode in the EDLC [11]. Comparison of the spectra for the EDLCs shows that the radii of the semicircles decrease inversely with the electrical capacitance. This result is related to the active area of the electrode. The key point is that all the EDLCs have a relatively low resistance compared with that of the Li/$SOCl_2$ cell (Fig. 2(b)).

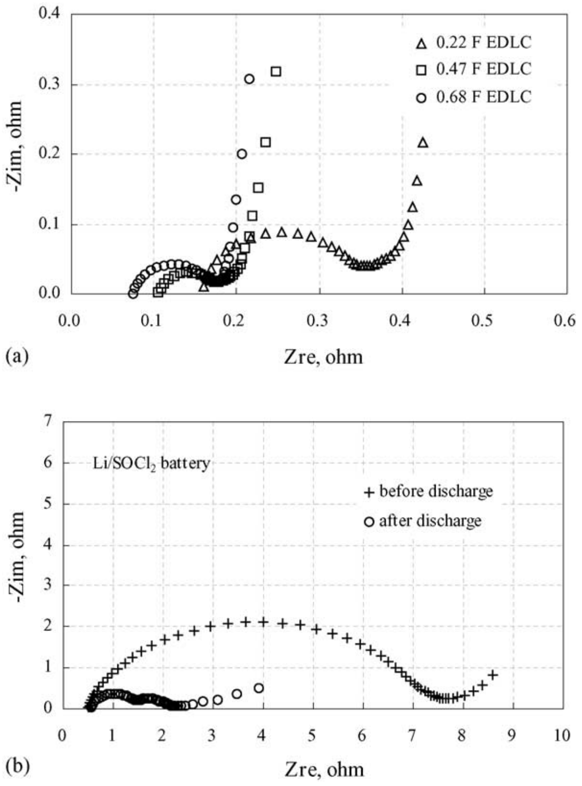

Fig. 2. Impedance spectra of: (a) 0.22, 0.47 and 0.68 F EDLCs and (b) Li/$SOCl_2$ bobbin-type battery.

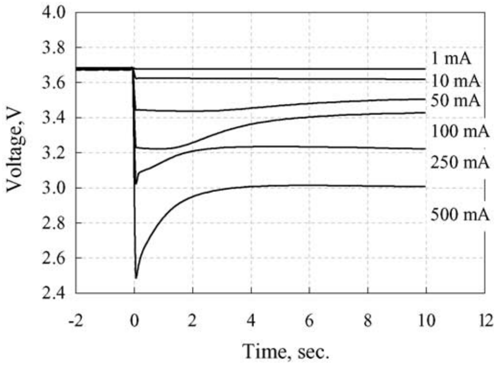

Fig. 3. Discharge curves of Li/SOCl$_2$ battery at discharge current rates of: 1, 10, 50, 100, 250 and 500 mA.

3.2. Voltage delay phenomenon of Li/SOCl$_2$ cell

The discharge curves of the bobbin-type Li/SOCl$_2$ cell at discharge-current rates of 1, 10, 50, 100, 250 and 500 mA are presented in Fig. 3. The voltage delay, i.e., the recovery time from the transient minimum voltage (TMV), is not observed when discharging with low current such as 1 and 10 mA. Rather, the delay starts faintly from 50 mA and is more clearly seen at over 100 mA. This phenomenon is well known in the battery fields [2–4] and is related to the formation of a passive layer on the surface of the lithium anode.

To explain the relation between the voltage delay and the passive layer, the impedance of the cell was investigated as a function of the cell state-of-discharge. The impedance spectra shown in Fig. 4 were measured at the points marked by arrows in the insert. The profile before discharge appears to be a large, depressed, and imperfect semicircle. This feature can be attributed to typical resister/capacitor coupling that is used to describe the effects of passive layers on the lithium anode. The depression appears to be composed of two semicircles reflected at two interfaces. One is from the interface of the lithium anode and the passive layer, while the other arises from the interface of the passive layer and the electrolyte. The diameter of the depressed semicircle is about 7 Ω, which is the anode resistance including the resistance of the passive layer. After discharging, the measured impedance has a small diameter and the shape is clearly separated into two semicircles. This low resistance and the separation are related to the breakdown of the passive layer on the surface of the lithium anode. This breakdown largely reduces the resistance of the lithium anode, which has a negligible value compared with the total resistance of the cell. By contrast, the resistance of the carbon cathode becomes more important than that of the anode. Therefore, the lithium anode no longer influences the measured impedance. The impedance spectra measured after discharging relates only to the resistance of the cathode. This cathode impedance also consists of two separated semicircles, which are due to the interface between the electrolyte and the passive layer and the interface between the passive layer and the electrode. On discharging, the passive film is broken and the cell voltage is recovered (see Fig. 4). Therefore, the recovery time is related to the breakdown rate of the passive layer on the surface of the lithium anode.

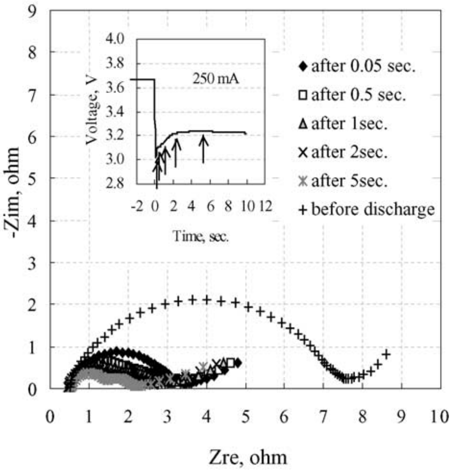

Fig. 4. Impedance spectra of Li/SOCl$_2$ battery as function of state-of-discharge; discharge time: 0.05, 0.5, 1, 2, and 5 s.

3.3. Voltage delay suppression of hybrid cells

The discharge curves of Li/SOCl$_2$ and hybrid cells at a constant current of 500 mA are given in Fig. 5. The Li/SOCl$_2$ cell experiences a voltage drop to a low level of approximately 2.5 V. The hybrid cells, however, exhibit a reduced the voltage drop. The higher the capacitance of the EDLC, the lower is the voltage drop at the high-rate discharge. In addition, the constant-current voltage (CCV) of the hybrid cells is somewhat decreased. These results can be explained as follows.

When the hybrid cells are discharged, the EDLC will be initially discharged faster than the Li/SOCl$_2$ cell due to the lower internal resistance as shown in Fig. 2. Therefore, the voltage drop is suppressed mainly due to the characteristics of the EDLC. At this moment, a voltage difference is established between the Li/SOCl$_2$ cell and the discharged EDLC so that the battery is being discharged at a very high current in order to charge the EDLC. As a result, the internal resistance of the battery is reduced by as much as that of the capacitor. The voltage of the hybrid cell is recovered and constant. During

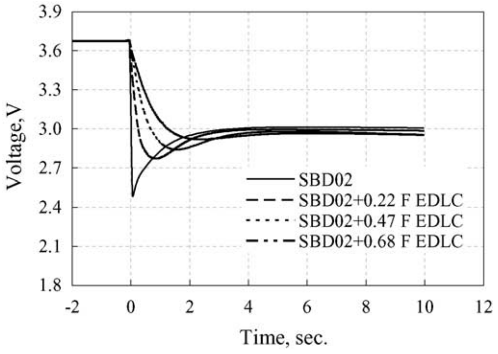

Fig. 5. Discharge curves of hybrid cells at constant current of: 500 mA.

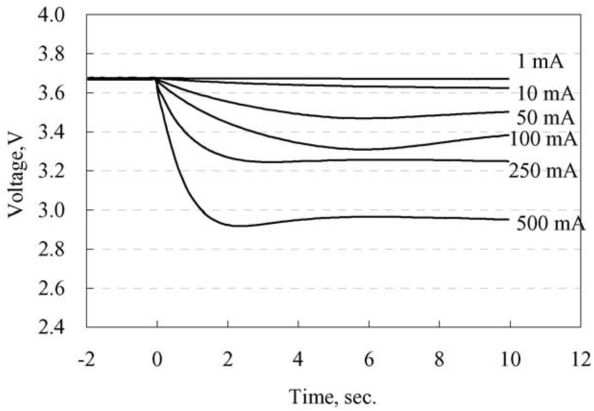

Fig. 6. Discharge curves of hybrid cell at discharge current rates of: 1, 10, 50, 100, 250 and 500 mA.

continuous discharge, the current output from the Li/$SOCl_2$ cell flows into the external load through the EDLC. Therefore, the CCV is somewhat decreased. To confirm this scenario, further detailed studies were conducted with a Li/$SOCl_2$ cell and a 0.68 F EDLC.

The discharge curves of the hybrid cell at various discharge rates are presented in Fig. 6. Compared with data for a Li/$SOCl_2$ cell, as shown in Fig. 3, the voltage delay is virtually suppressed at all discharge rates. The hybrid cell has sufficient time to break the passive layer during discharge. The EDLC operates as current buffer device for very high-rate discharge.

In order to explain the scenario in Fig. 5 clearly, the impedance of the hybrid cell was investigated in detail. The hybrid cell was discharged at 250 mA via the electrical circuit shown in Fig. 7(a). In order to measure the impedance, the Li/$SOCl_2$ cell was separated from the EDLC (Fig. 7(b)). In this case, the measured impedance depends on only the state of the Li/$SOCl_2$ cell. The resulting impedance spectra are shown in Fig. 8. Compared with Fig. 4, the impedance hardly changes until 1 s after discharging and then it is largely reduced after 2 s. This means that the passive layer of the Li/$SOCl_2$ cell with the EDLC has not been broken during the initial discharge. At these stages, only the EDLC was discharged. With further discharge, however, the Li/$SOCl_2$ cell starts to discharge rapidly in order to charge the EDLC. It is then that the passive layer of the lithium anode is broken and is the reason why the impedance after 2 s is remarkably reduced (Fig. 8). Therefore, the EDLC operates as current buffer device for very high-rate discharge.

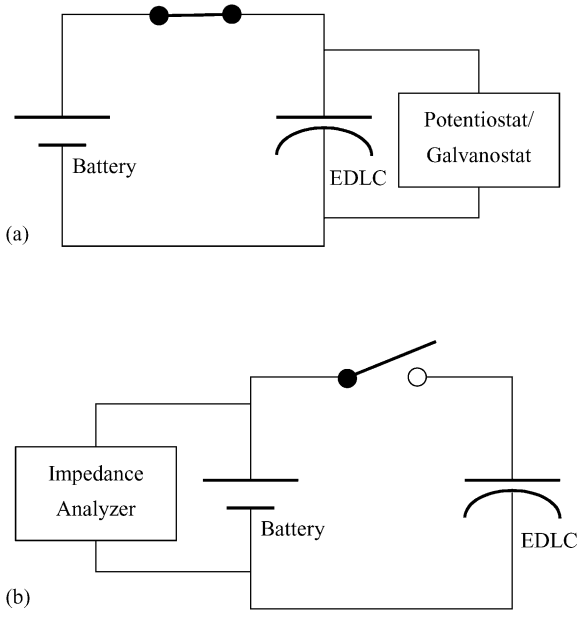

Fig. 7. Electrical circuits prepared to investigate impedance of Li/$SOCl_2$ battery of hybrid cell.

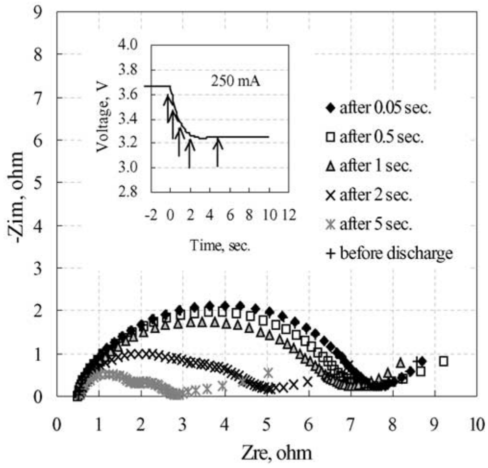

Fig. 8. Impedance spectra of hybrid cell as function of state-of-discharge; discharge time: 0.05, 0.5, 1, 2 and 5 s.

3.4. Application of hybrid cell

A simple current profile for high current pulse applications is shown in Fig. 9. The electrical current consumption includes a sustained low background current of 1 μA for 10 s and intermittent short current pulses with amplitude of 500 mA for 1 s. This signal was applied to both a Li/$SOCl_2$ cell and a hybrid cell, the results are given in Fig. 10. The

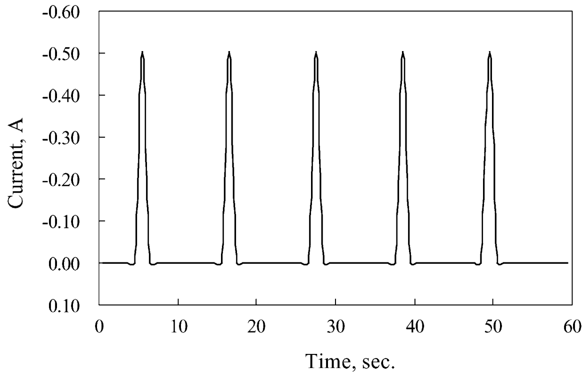

Fig. 9. Simple high-current pulse profiles.

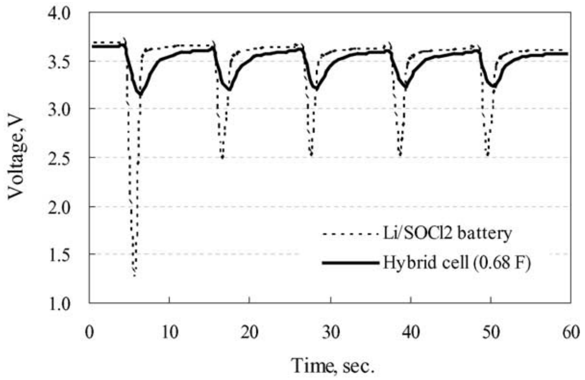

Fig. 10. Voltage vs. time of Li/SOCl$_2$ battery and hybrid cell subjected to the pulse of profiles shown in Fig. 9.

voltage of the Li/SOCl$_2$ cell declines severely at high current pulses compared with that of hybrid cell. Moreover, the initial voltage drop is more severe due to the passive layer on the lithium anode. For a hybrid cell, the EDLC operates as current buffer against the high current pulse. Therefore, the voltage drop is suppressed and the passive layer is broken. The hybrid cell treated in this paper is suitable for high-current pulse (under 1 s) applications.

4. Conclusions

The Li/SOCl$_2$ cell has a voltage delay problem at high current pulses. In order to overcome this disadvantage, the cell has been connected in parallel with an EDLC. The electrical characteristics of the resulting hybrid cell have been investigated by several electrical techniques. The hybrid cell does not suffer a voltage delay at high current pulse discharge. In spite of the high resistance of the passive layer, the hybrid cell discharges without the delay. The discharge mechanism of the hybrid cell has been investigated by impedance spectroscopy with the Li/SOCl$_2$ cell separated from the EDLC. The results show that the EDLC operates as a high-current buffer for high-rate discharge. Therefore, the Li/SOCl$_2$ bobbin-type cell connected to an EDLC can be applied for high-current pulse (under 1 s) applications.

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