

ASSEMBLY AND TESTING OF LITHIUM-ION CAPACITORS

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Introduction

Commercially available electric double layer capacitors (EDLCs) having symmetrical high-surface area activated carbon (AC) electrodes are promising energy storage devices. They are capable of delivering high power in short periods of time for use in a variety of applications from digital electronics to electric vehicles. However, a limitation of these devices is their low energy storage/delivery capability relative to advanced batteries. One promising approach to improve the energy storage capability of EDLCs is to replace the negative AC electrode with an intercalation graphite electrode that has high energy density; the so-called “lithium-ion capacitor” (LIC). LICs are observed to be capable of storing about 5 to 10 times more energy compared with EDLCs and have high power and long cycle-life similar to EDLCs [1-4].

In order to take advantage of the high charge storage capacity of graphite (372 mAh/g for graphite vs. ~ 40 mAh/g for AC) and its high negative potential (~ 0.1 V vs. Li/Li+) in an LIC, graphite is pre-doped with lithium-ions using a sacrificial lithium metal. The performance of a pre-doped LIC is evaluated at various charge/discharge current rates and at two different cell cut-off voltages.

Experimental

Commercial graphite (SLP30, Timcal Ltd.) and activated carbon (Maxsorb) materials were used as received. The graphite and activated carbon electrodes were prepared by coating a mixture of: graphite or activated carbon, a conductive carbon black (Timcal Super P) and carboxymethyl cellulose salt binder (CMC) dispersed in water, onto 30 µm copper foil (for graphite) or aluminium foil (for activated carbon) using a grooved-rod applicator at a thickness of 60 µm (for graphite) or 100 µm (for activated carbon). All coated electrodes were roll-pressed and dried at 100 °C overnight under dynamic vacuum before testing.

The electrochemical performance of the LICs were evaluated using 3-electrode cells and the potentials of the positive and negative electrodes of the LICs were measured versus Li/Li⁺. The coated graphite and activated carbon electrodes were punched into 13 mm diameter discs and sandwiched either side of an electrolyte-soaked polypropylene separator (Solupor, 25 µm) before assembly into a 3-electrode cell. A piece of lithium metal was incorporated into the cell and was used for both pre-doping the graphite and monitoring the potential swings of positive and negative electrodes during the LIC charge/discharge. The electrolyte consisted of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC) mixture (1:1:1 by volume) containing 1M

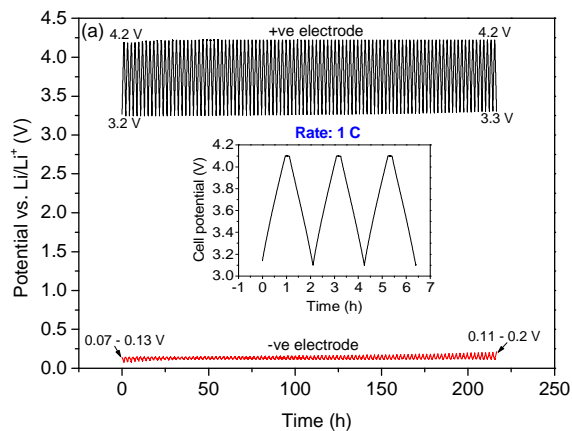
LiPF₆ salt (Sol-Rite, Mitsubishi Chemical Corp., Japan). All cells were assembled in an Argon-filled glove box. After the electrolyte addition, lithium-ion pre-doping into the graphite was achieved by short circuiting the Li metal and graphite electrodes overnight.

The cells were galvanostatically charged/discharged at various C-rates between the cut-off voltages of either 3.1 - 4.1 V or 2.0 - 4.1 V. A constant voltage float of 4.1 V was applied for 10 min (during 1 C cycling) or 5 mins (during 10 C cycling) when the cell voltage reached 4.1 V during charging but no constant-voltage float applied at the end of discharged state. All the LICs were initially conditioned by cycling at a C-rate of C/10 (10 hour charge/discharge) between the cut-off voltages for 3 cycles before gathering the cell performance data. Masses of both the active material and the conductive carbon additive (Super P) were used for the cell energy density calculation.

Galvanostatic charge/discharge cycling of the LICs were performed using a Maccor (Series 4000) battery cycler. All the electrochemical tests were performed at ambient temperature.

Results and Discussion

The cycle-life behaviour of a typical LIC cycled at the cell-cut off voltage of 3.1 – 4.1 V and with a current rate of 1 C is shown in Fig. 1. With continuous cycling, a ~ 0.1 V positive shift in the potential swings of both the positive and negative electrodes are observed (Fig. 1(a)). Consequently, the slight energy density decrease on cycling (Fig. 1(b)) is due to the decreased utilisation of the positive electrode material (~ 0.1 V reduction in potential swing, from 3.2 – 4.2 V to 3.3 – 4.2 V, Fig. 1(a)). This reduction in the positive electrode swing window on cycling is caused by a positive potential drift of the negative electrode (0.07 – 0.13 to 0.11 – 0.2 V). The positive drift of the negative electrode potential with cycling indicates that there is an apparent “leakage of charge” (i.e. Li-ion de-intercalation akin to self-discharge). The initial discharge energy density of the cell is calculated to be ~ 55 Wh/kg and retained about 97% of this value after 100 cycles (Fig. 1(b)).



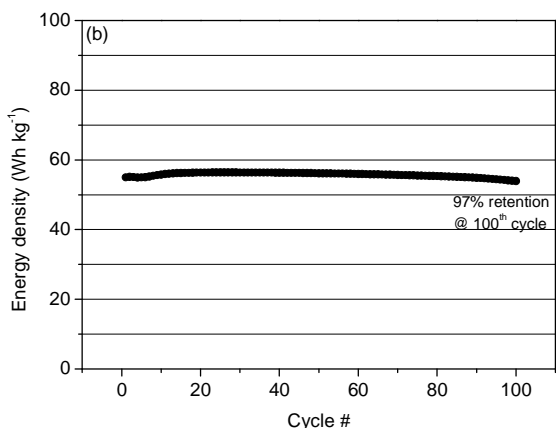


Fig. 1 Cycle-life behaviour of a lithium-ion capacitor showing the (a) positive (activated carbon) and negative (pre-doped graphite) electrode potential swings and (inset) the cell potential change during the charge/discharge cycling and (b) energy density (based on the weights of both electrode active materials) as a function of cycle number. Charge/discharge rate: 1 C. Ratio of positive to negative electrode active material is 0.87.

In the LIC device during charging, anions (PF_6^- from the electrolyte) adsorb on the positive electrode surface and cations (Li^+ from the electrolyte) intercalate into the pre-doped negative electrode. During discharge, anion desorption and cation de-intercalation occurs from the respective electrodes. At the completely discharged state (cell voltage of 3.1 V), the positive electrode (AC) is in a neutral state, whereas the negative electrode still contains the pre-doped Li-ions and explains why the negative electrode potential stays nearly constant during the charge/discharge.

One of the main advantages of pre-doping the negative electrode in LIC lies in maximising the discharge energy density of the cell by making the positive electrode swing across a larger potential window. This has been examined by decreasing the discharge cut-off voltage of the cell to 2.0 V and the results obtained are shown in Fig. 2. It is seen that the delivered energy density of the cell has nearly doubled (compared with Fig. 1) by lowering the cell cut-off voltage, which in turn is due to the extended potential swing of the positive electrode. During discharge, the anion desorption process at the AC electrode is completed at around 3.2 V (vs. Li/Li^+), and below 3.2 V, cation (Li^+) adsorption begins, which is supplied from the pre-doped negative electrode. However, at this low cell cut-off voltage, the negative electrode cell potential is seen to drift rapidly towards positive potentials upon continuous cycling. After 100 cycles, the cell retains only 77% of the initial discharge capacity. A good correlation of decrease in cell capacity with the reduced potential swing window of the positive electrode is clearly seen.

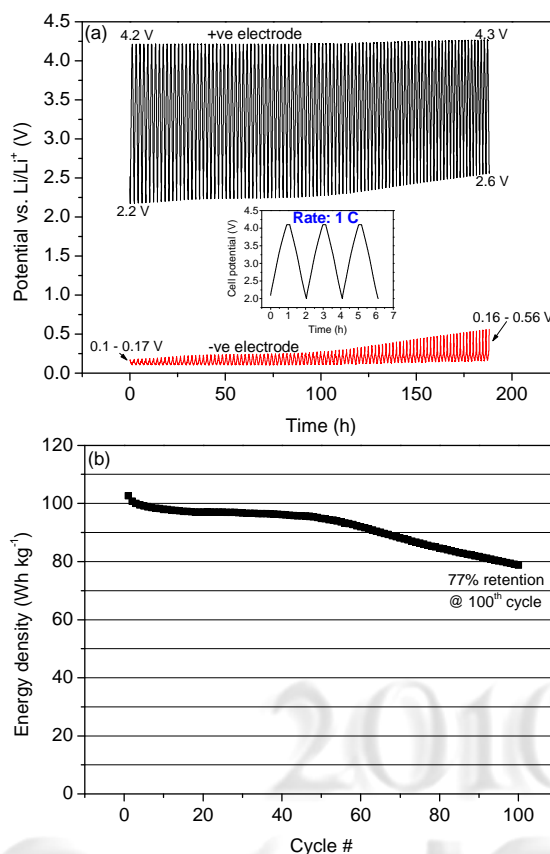


Fig. 2 Same caption as for Fig. 1.

Conclusions

LIC assembled with pre-doped graphite and activated carbon electrodes delivers a 4 to 8 times higher energy density than an EDLC when cycled in the potential window of 3.1 – 4.1 V or 2.0 – 4.1 V, respectively. The positive drift in the potential of the pre-doped graphite electrode on cycling is the root cause of the energy density fade in the LIC. Modification of the conventional graphite negative electrode material and/or changes in Li-ion pre-doping methodology are expected to offer better stability of the negative electrode thereby to improve the cycle-life performance of the LIC device.

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References

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