

Study of Li-ion Capacitors' Cycle Performance

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Lithium (Li)-ion Capacitors (LIC) have attracted more and more attention as a new power source recently because they can achieve higher power density than Li-ion batteries and they have higher energy density than the conventional double layer capacitors. We reported a LIC with activated carbon cathode and hard carbon/stabilized lithium metal powder (SLMP) anode electrodes with high energy density, high power density and long cycle life.^{1,2} In this novel structure, the SLMP was applied onto the surface of the anode hard carbon electrodes to provide necessary ions in order to satisfy the charge capacities of both electrodes and also lower the potential of the anode so that the open circuit voltage of the cell could be higher.

The cyclic stability of anode was studied using a half cell configuration, which was composed with activated carbon working electrode and Li counter/reference electrodes. These half cells were charged and discharged with a fixed low potential of 2.0 V vs. Li/Li⁺; however, a different high potentials from 4.1 to 4.5 V vs. Li/Li⁺. The cyclic stability of cathode was studied using "full cell" configuration, which was composed with activated carbon cathode and hard carbon/SLMP anode; however, the mass ratio between anode and cathode varied from 1.2 to 2.3. The cell was cycled from 2.0 to 4.1 V for over 1000 cycles. A Li/Li⁺ reference electrode was inserted into the cells in order to monitor potentials of each electrode. The separator was a microporous membrane (Celgard 3501). The electrolyte was 1 M LiPF₆ in ethylene carbonate:dimethyl carbonate at a weight ratio of 1:1.

Fig. 1 shows the cycling performance of the half cells with activated carbon working electrode and Li counter electrode under different charge and discharge potential. It can be seen that in the first 100 cycles, there is no significantly degradation in the discharge capacitance for all cathodes charged to up potential 4.1 to 4.5 V vs. Li/Li⁺; however, after 200 cycles, the cathode charged to 4.5 V vs. Li/Li⁺ showed a clear degradation in the capacitance.

Fig. 2 shows the cycling performance for cells with different cathode and anode electrodes' mass ratio. It can be seen that more cathode material resulted greater degradation of capacity. SEM images showed that there was the solid electrolyte interface (SEI) growth at the surface of hard carbon and the growth rate increased with increasing the mass ratio.

Fig. 3 shows the galvanostatic charge-discharge profile from the four 3-electrode test which were cycled between 2 to 4.1 V. It can be seen that the activated carbon cathode reached the maximum potential in the range of 4.3-4.1 V vs. Li/Li⁺, which is in the stable range as found in the previous half cells cycling results. The lowest potentials of the hard carbon anode were 0.18, 0.1, 0.05 and 0.02 V vs. Li/Li⁺ for the Cell1.2, Cell1.4, Cell1.9 and Cell2.3, respectively. As the cell mass ratio of the cathode to anode increases, the lowest potential of the anode decreases which resulted in the faster accumulations of the thick SEI layers at the surface of the hard carbon.

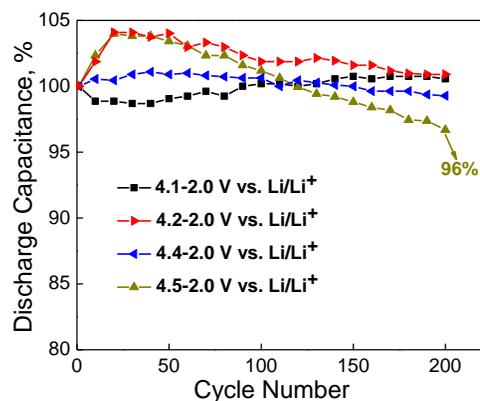


Fig. 1 Cycling performance of the half cells with activated carbon working electrode and Li counter electrode under different cycle potential.

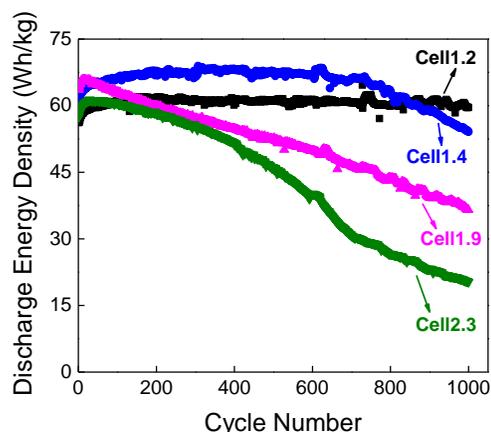


Fig. 2 Cycling performance for cells with cathode and anode mass ratios of 1.2, 1.4, 1.9, and 2.3 for Cell1.2, Cell1.4, Cell1.9 and Cell2.3, respectively.

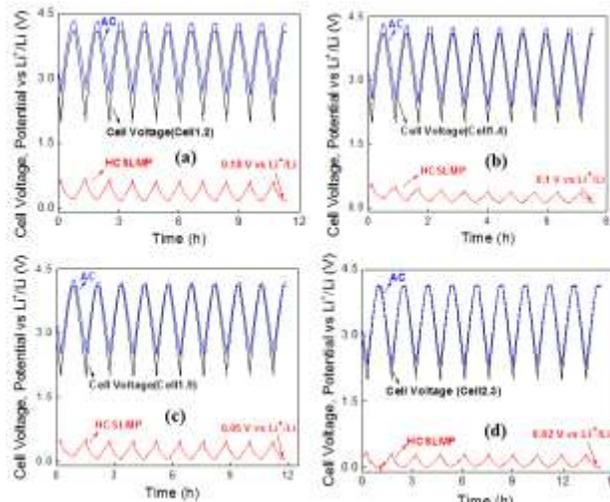


Fig. 3 Galvanostatic charge-discharge profiles measured from (a) Cell1.2, (b) Cell1.4, (c) Cell1.9, and (d) Cell2.3.

References

- J.P. Zheng and W.J. Cao, The 20th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Florida Educational Seminars Inc. (2010).
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