



Effect of carbon types on the electrochemical properties of negative electrodes for Li-ion capacitors

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ABSTRACT

The electrochemical properties of various carbon materials (graphite and hard carbon) have been investigated for use as a negative electrode for Li-ion capacitors. The rate capabilities of the carbon electrodes are tested up to 40C using both half and full cell configurations. It is found that the capacitance of the hard carbon material at 40C could be maintained up to 70% of that at 0.2C in full cells with an activated carbon positive electrode, which is the best among the carbon materials. The cycle performance of the hard carbon demonstrates that the initial capacitance is retained up to 83% even after 10,000 cycles. The outperforming results could be ascribed to the microstructure of hard carbon, which indicates that hard carbon is more suitable as negative electrode materials for high power energy storage applications.

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1. Introduction

Recently, hybrid electrochemical capacitors (HECs) have been proposed as a member of advanced capacitors. These HECs consist of a faradaically rechargeable (battery type) electrode and a polarizable (typical capacitor type) electrode. They are called as an asymmetric capacitor as well because of their different charge/discharge profiles resulted from the unique reaction mechanisms of each electrode. The nice features of HECs are a high energy density over electric double layer capacitors (EDLCs) and a high power density over battery systems. Among HECs, the lithium ion capacitor (LIC) is composed of a lithium-doped carbon negative electrode and an activated carbon positive electrode, which is half a lithium ion battery (LIB) and half an EDLC. With LICs, it would be possible to aim at much larger energy density (more than three times) than EDLC without sacrificing the advantages of capacitors over batteries. Because of its competitive characteristics it is expected to be useful power sources for hybrid electric vehicles (HEVs) and electric vehicles (EV) [1–4].

In a LIC, the swing of lithium ion occurs in the carbon negative electrodes while anion ad/desorption reaction happens on the surface of the activated carbon positive electrode. The intercalation reaction is much slower than the surface ad/desorption reaction in general. Therefore, the characteristics of negative electrode

materials will govern the power capability of LICs. The durability of activated carbon has been proven by EDLC for such a long cycle life (more than a few hundred thousand cycles) while most of carbon materials have been characterized only for a few hundred cycles in the LIB industry. There are many types of carbon materials that could be used for the negative electrode material. Some previous papers have reported the characteristics of carbon materials in a specific view [5–9].

In this work, we have investigated the electrochemical properties of the most representative carbons such as natural graphite, artificial graphite, and hard carbon as the negative electrode materials for LICs with various points of view. The characteristics of carbon materials have been fully evaluated in designable energy, high rate capability, and cycle durability for LIC applications using four- and two-electrode systems.

2. Experimental

Commercial active materials were used for both positive and negative electrodes as received. Detailed characteristics of these materials are summarized in Table 1. A positive electrode (PE) was prepared by coating the mixture of activated carbon (MSP20), a carbon additive (Super P), and poly(vinylidene difluoride) (PVDF) as a binder by 80:10:10 mass ratio on an Al mesh. For the negative electrode, three types of different carbons (artificial graphite-MAG-Hitachi, natural graphite-DAG-Sodiff, and hard carbon-Carbotron-Kureha) were used for active materials. Negative electrodes (NE) were prepared by the same

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Table 1
Characteristic data of various carbon active materials for the negative electrode of Li-ion capacitors.

Name	Particle size (μm)	BET ($\text{m}^2 \text{g}^{-1}$)	Tab density (g cm^{-3})	Discharge capacity (mAh g^{-1})	Initial efficiency (%)
MAG	21	3.2	0.61	350	92
DAG	18	2.3	1.01	352	94
Carbotrons	10	2.3	0.86	213	79

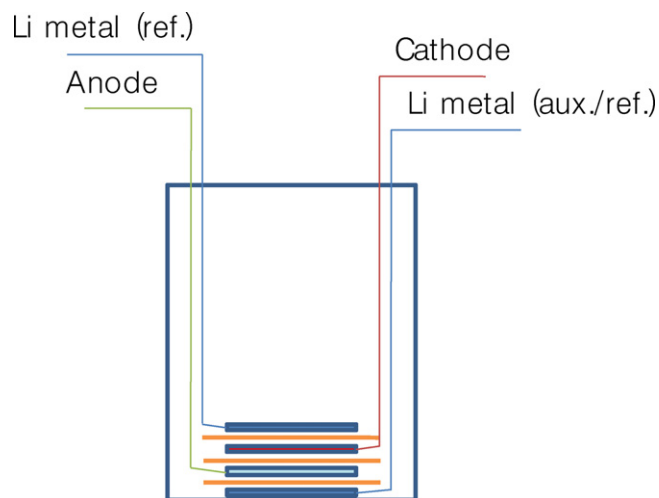


Fig. 1. Schematic diagram of the four-electrode cell made of a glass beaker.

method that was used for the PE except active materials (various carbons), the ratio of mixture (70:20:10), and a Cu mesh. Coated electrodes were punched out in 12 mm (PE) and 14 mm (NE) diameter pieces, respectively. The active loading level of NE was 1.5 mg cm^{-2} (MAG and DAG) and 2.4 mg cm^{-2} (Carbotron) while the one of PE was varied to obtain optimized cell design parameter.

The electrochemical measurements were carried out by using two types of lab designed glass cells; a two-electrode cell for the carbon NE tests and a four-electrode cell for the full cell tests as shown in Fig. 1. A lithium metal foil (170 μm thick, Hosen) was punched out in 14 mm diameter disc for a counter electrode (CE) in a two-electrode cell and reference electrodes (RE1 and RE2) in a four-electrode cell. The electrolyte solution was 1 M LiPF_6 in 3:7 ethylene carbonate/diethyl carbonate (EC/DEC) (PANAX ETEC). All two-electrode cells (Li vs. carbons) were conditioned by cycling at 0.1C rate (10 h charge/10 h discharge) between the cut-off voltage of 0.01 and 1.5 V (3 cycles) before any electrochemical tests. The cells were cycled with constant current (CC)–constant voltage (CV) charging condition which charges cells galvanostatically to cut-off voltage (0.01 V vs. Li/Li^+) followed by potentiostatic charge until the current reaches 1% of the cell capacity. The characteristics of LICs were measured using four-electrode cells. Pre-doping process was carried out under the constant voltage condition of 10 mV (RE2 vs. NE) for 1 h. Initial conditioning was performed by cycling at 0.1C rate between the cut-off voltage of 1.4 and 4.3 V (3 cycles, PE vs. NE). All electrochemical tests were performed using a battery tester (MACCOR Series 4000 System) at ambient temperature in a dry room, the controlled dew point of which was lower than -55°C .

Field-emission scanning electron microscopy (FE-SEM) (JSM-7000F, JEOL) was used to observe the morphology of the carbon materials. Particle size and Brunauer–Emmett–Teller (BET) surface area/pore size distribution of active materials were measured using Malvern particle size analyzer and Micromeritics ASAP 2000, respectively.

3. Results and discussion

The FE-SEM images of the carbon materials are displayed in Fig. 2. It is observed that the graphite (MAG and DAG) samples have potato-like morphologies with smooth surface while the hard carbon (Carbotron) sample shows an irregular shape with sharp edge. In case of the graphite, small flakes observed in an enlarged image indicate that the morphology control process has been applied to produce this powder. It seems that the process level of perfection on the DAG is higher than that on the MAG since the DAG has more homogeneous potato shape if both samples have been through the similar process. Unlike the graphite, hard carbon does not have a common shape with well developed edges, which indicates it was pulverized without any further treatment after. The physical parameters including average particle size and BET surface area of the samples are summarized in Table 1 and the pore size distribution of the materials is shown in Fig. 3.

Fig. 4 presents the voltage profiles of the carbon electrodes for the first cycle. All three materials show their characteristic electrochemical behavior on the reaction with lithium. For the two graphite electrodes (Fig. 4(a and b)), reversible capacities of about 350 mAh g^{-1} are delivered with initial coulombic efficiencies of 92–94%, which are close to the theoretical capacity of graphite (372 mAh g^{-1}). During the first discharge process (Li intercalation in half cell configuration with Li metal), the electrodes have sloping profiles from 0.8 to 0.15 V (vs. Li/Li^+), which are related to the formation of solid electrolyte interphase (SEI) films. It is well known that the SEI film plays a role to protect the graphite surfaces for further cycles although it irreversibly consumes some amount of charges [8]. Below 0.15 V, relatively flat plateaus are observed, which indicates stepwise Li intercalation into graphite. This staging phenomenon can be explained by noting that the stage index, which is the number of graphene layers between two nearest guest (Li) layers, is gradually decreasing through each plateau. The plateaus indicate two-phase reactions, which mean the coexistence of different two phases at each stage [8]. In the subsequent charge process, plateaus are also observed at around 0.2 V for both electrodes, which demonstrates that the reversible Li de-intercalation from graphite occurs. On the other hand, the hard carbon electrode has a reversible capacity of ca. 213 mAh g^{-1} with an initial coulombic efficiency of 79% (Fig. 4(c)). The voltage profile of the hard carbon electrode differs greatly from those of graphite electrodes. The intercalation of Li^+ begins at 1.2 V and the curve is sloping down without showing any noticeable plateau. This typical feature could be attributed to the disordered crystal structure of hard carbon [8–12]. Hard carbon materials generally have the disordered structure consisting of cross-linked carbon sheets (graphene layers), which leads high irreversible capacities, sloping profiles, and high rate capability. It was reported that the sloping voltage profiles are favorable for fast Li^+ insertion/deinsertion [10,11] and easy monitoring of state-of-charge in cells [12].

The rate characteristics of the carbon electrodes are plotted as a function of the C-rate in Fig. 5. The gravimetric de-intercalation capacities were normalized against that of the same electrode at the slowest C rate (0.2C). For the graphite samples, as the C rate increases the capacity retention decreases drastically after 10C. In contrast, the normalized capacity of the hard carbon electrode is maintained pretty well up to 20C rate. It can be ascribed to the

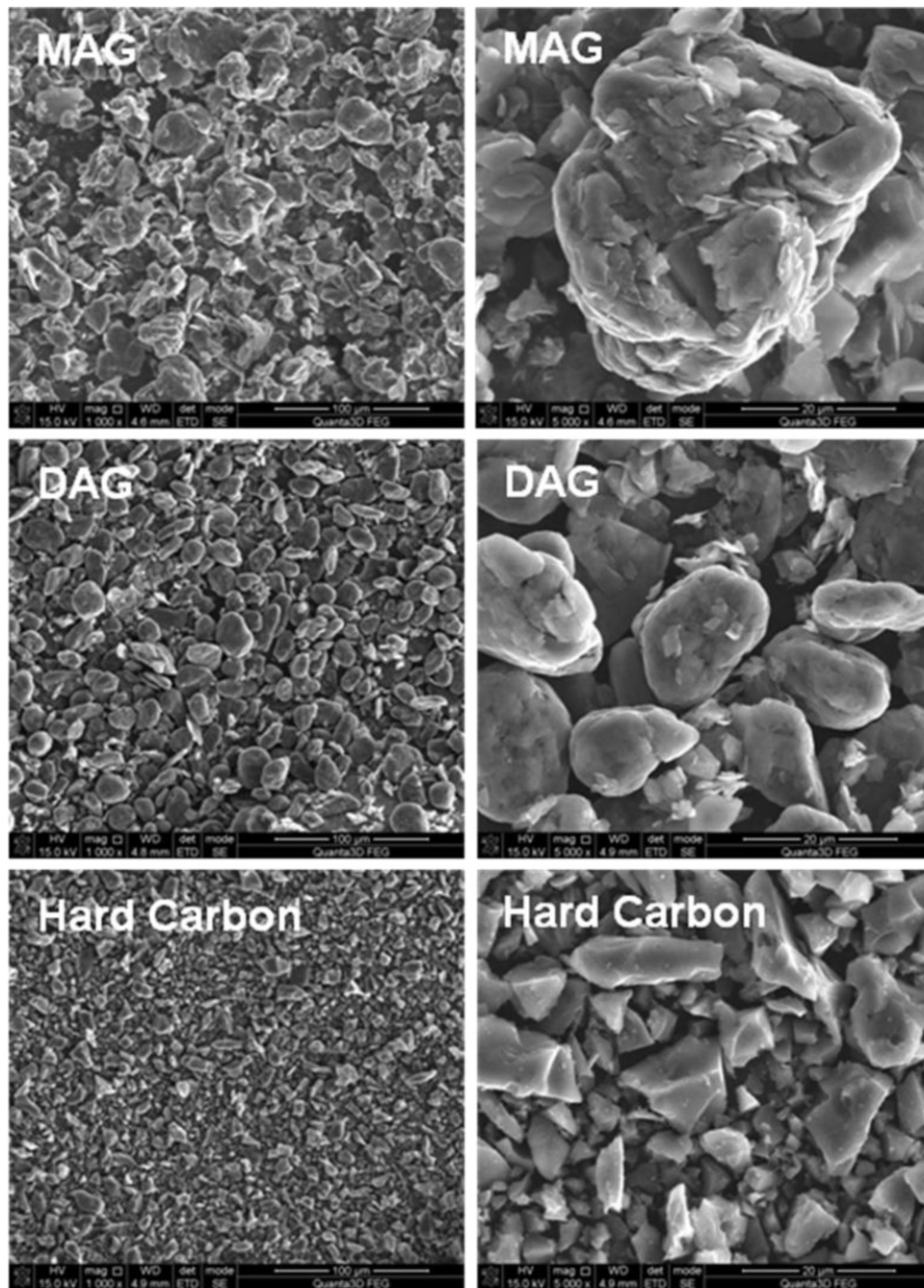


Fig. 2. FE-SEM images of various carbon powders; MAG, DAG, and hard carbon.

microstructure of the carbons. Hard carbon is comprised of smaller pieces of carbon (graphene) layers than those of graphite, which results in enabling a faster solid ionic diffusion process in carbon lattices [8,11,12]. Thus, it is found that the rate capability of hard carbon outperforms that of graphite materials. And it seems that the physical parameters of the commercial carbon materials such as particle size, BET surface area, and pore size distribution are not very influential at the high rates.

To characterize the full cell performance of these carbon materials, electrodes were designed based on gravimetric capacity of active materials. For the asymmetric capacitors, the two-electrode full cell capacitance, C_{cell} (F g^{-1}) is expressed below [13]:

$$(C_{\text{cell}}W_{\text{cell}})^{-1} = (C_{+}W_{+})^{-1} + (C_{-}W_{-})^{-1} \quad (1)$$

where W is the mass of the active materials (g), $W_{\text{cell}} = W_{+} + W_{-}$, and the subscripts, + and – mean positive and negative electrodes, respectively. The theoretical cell capacitances were calculated as a function of the mass ratio (MR), $W_{+}/(W_{+} + W_{-})$, using the half cell capacitances of the MSP20 cathode material and the carbon anode materials. As shown in Fig. 6, the simulation results are presented, where the specific capacitances are 156 F g^{-1} for the MSP20 cathode, 264 F g^{-1} for the hard carbon (Carbontron) electrode, 434 F g^{-1} for MAG, and 437 F g^{-1} for DAG (potential range: 1.4–4.3 V). The maximum cell capacitance was achieved in the range of $W_{+}/(W_{+} + W_{-}) = 0.55\text{--}0.65$, which shows typical asymmetric behaviors while a symmetric EDLC has the value of $W_{+}/(W_{+} + W_{-}) = 0.5$. The mass ratio range for maximum cell capacitance was selected to investigate the characteristics of full cells for each carbon material.

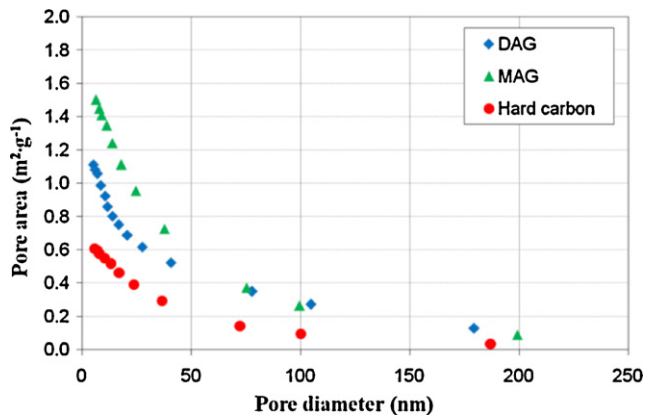


Fig. 3. Pore size distribution of various carbon powders; MAG, DAG, and hard carbon.

Fig. 7 shows various discharge voltage profiles for the cells fabricated with different carbon electrodes. Three voltage profiles for each cell were presented where the profiles are from a full cell (left side), a positive electrode (right upper), and a negative electrode (right lower). The four-electrode cell configuration was used, which has an individual reference electrode to a positive and a negative electrode, respectively. The discharge profiles were recorded for various electrodes which have different mass ratios of positive and negative electrodes. As shown in Fig. 7(a and b), graphite materials have the similar behavior each other. When the amount of the positive active material (activated carbon) is relatively small, the shapes of the profiles depend on those of positive electrodes because the discharge current is limited by the amount of activated carbon. As the relative amount of the positive active material increases to more than 0.65 in the mass ratio, the voltage curves are affected by the electrochemical behavior of the negative active materials, which have abrupt changes of profiles at the end of discharge. The mass ratio of both electrode materials is found to have an influence on the electrochemical behavior of Li-ion capacitors. When the hard carbon material is employed as negative electrodes in the full cell test, the voltage curves are presented in Fig. 7(c). The tendency of the profile variation is similar to the graphite materials. When the mass ratio is greater than 0.63, the curve shape of the hard carbon is reflected on the profiles of the full cells. It is obvious that the mass ratio of positive and negative electrodes is important for controlling the electrochemical behavior of Li-ion capacitors. The optimum ratios for cell capacitance could be tailored under the consideration of cell operating voltage.

To compare the rate capability of the carbon materials, the retention ratio of the capacitance values is plotted as a function of C-rate in Fig. 8. The capacitance was normalized with respect to the C-rate of the same electrode at the slowest rate of 0.2C in this study. For the electrodes having the mass ratio of 0.63, the graphite materials (MAG and DAG) show 26–29% retention at 40C while the capacitance of the hard carbon is maintained up to about 70% at the same rate. The better rate capability of the hard carbon electrode could be attributed to the disordered microstructure consisting of cross-linked carbon layers, which may lead fast Li^+ insertion and extraction processes. It was reported that the amorphous nature and isotropic texture of hard carbons are advantageous for high power Li-ion batteries [12]. This rate characteristic of hard carbon is also more favorable for high power Li-ion capacitor applications compared to graphite materials.

The Ragone plots for the full cells are illustrated in Fig. 9, which were obtained by calculating the power and energy density from the rate capability results. The mass of both electrode (cathode and anode) active materials is only considered for the calculation. As

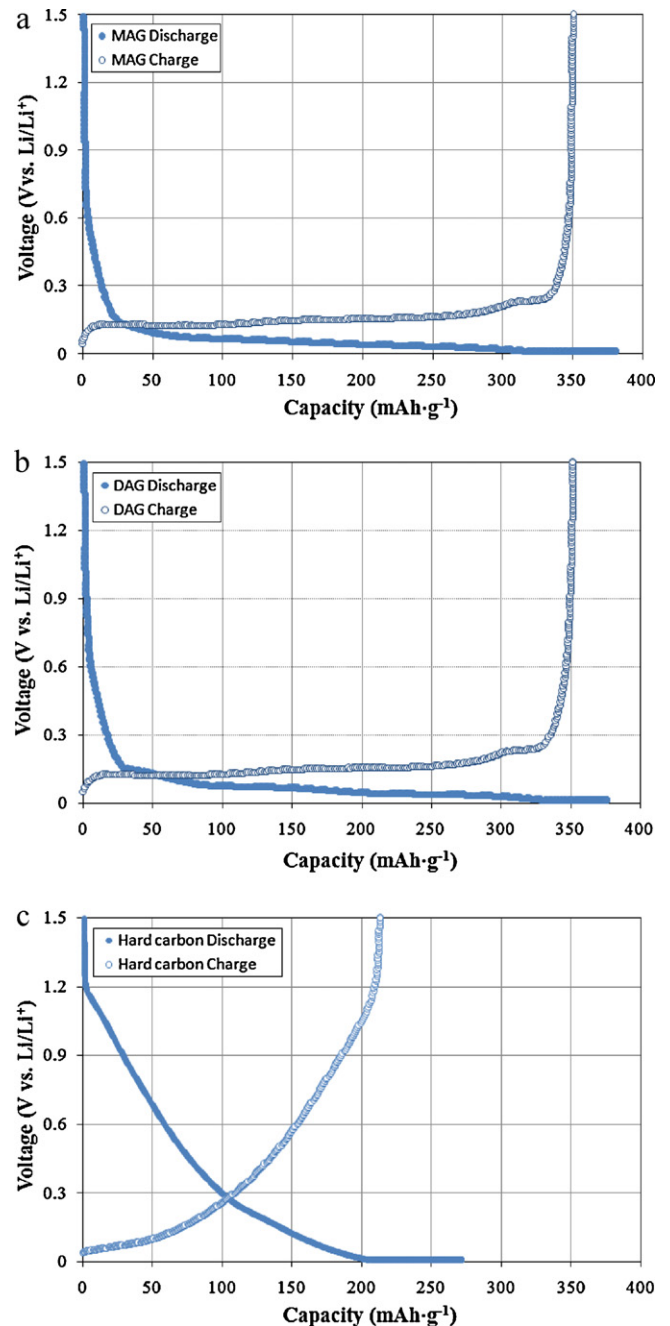


Fig. 4. Voltage profiles for electrodes prepared with (a) MAG, (b) DAG, and (c) hard carbon as active materials during initial charge (Li intercalation) and discharge (deintercalation).

expected, at the low power density range of $10\text{--}1000\text{ W kg}^{-1}$, the full cells employing graphite anodes have better energy density at the same power density because the anodes have higher capacitance at the low rates. With increasing power density, the cells having hard carbon anodes demonstrate better power and energy density owing to the rate characteristics of hard carbon.

Fig. 10 shows the cycle performance of the full cells employing activated carbon as a positive electrode material and various carbon materials (graphite and hard carbon) as a negative electrode material. All the cells were tested in the voltage range of 1.5–3.9 at 10C rate. The comparison of three materials reveals that the hard carbon has the best cycle life performance up to 10,000 cycles in terms of the capacitance retention. It is found that the capacitance of the hard carbon material could be retained

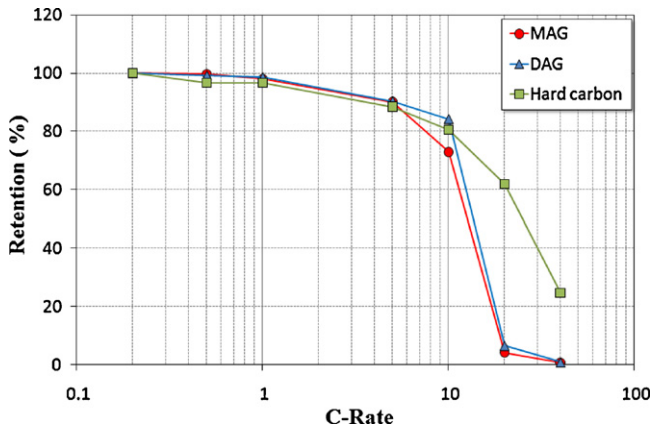


Fig. 5. Rate characteristics of the carbon electrodes evaluated with half-cell configuration.

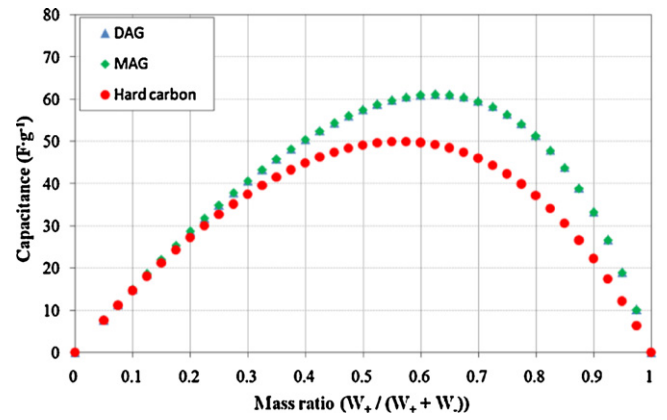


Fig. 6. Comparison of simulated cell capacity.

up to about 83% while the graphite materials (DAG and MAG) has the retention ratios of about 41 and 29% after 10,000 cycles, respectively. It indicates that the microstructure of hard carbon is more stable after the long term cycling, which enables to meet a requirement for capacitors. Based on the evaluation of the

electrochemical properties (rate performance and cycle life) of various carbon materials, it is concluded that the hard carbon material is more suitable as a negative electrode material for high power Li-ion capacitors.

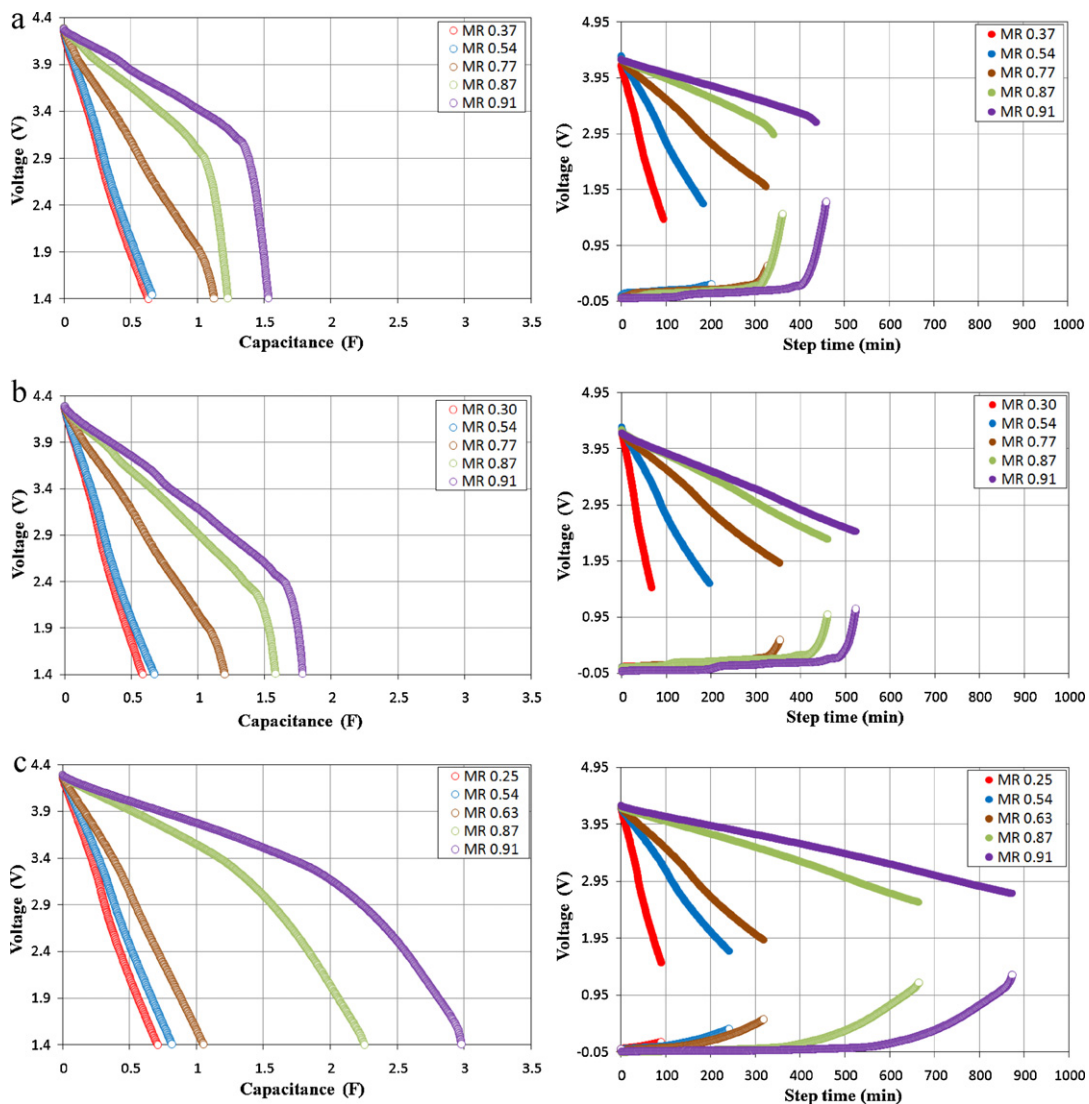


Fig. 7. Changes in the voltage of four-electrode cells having different types of carbon anodes: (a) MAG, (b) DAG, and (c) hard carbon.

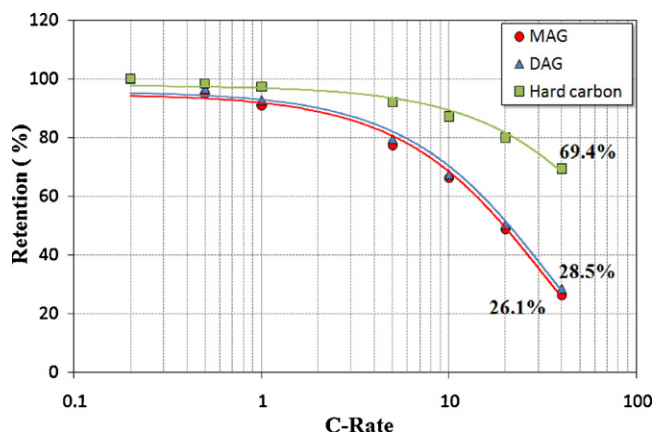


Fig. 8. Rate capability of full cells employing various carbon anodes.

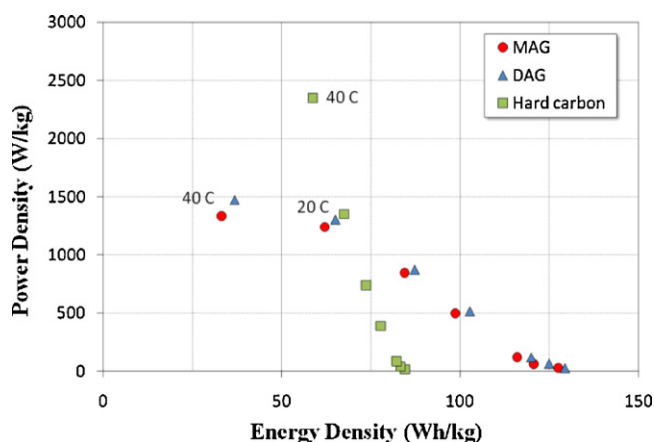


Fig. 9. Ragone plots of power density vs. energy density for full cells employing various carbon anodes.

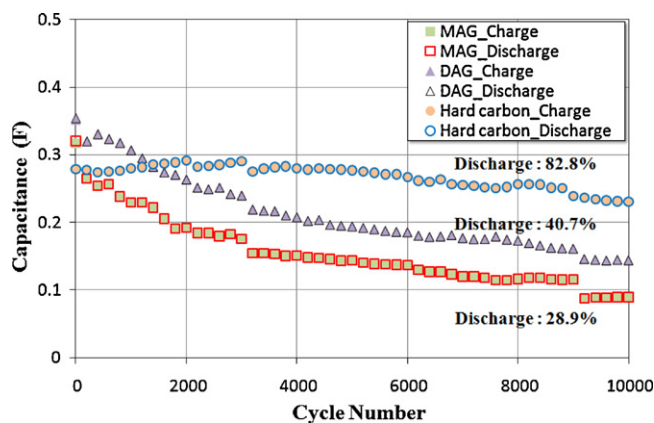


Fig. 10. Cycle performance of full cells employing various carbon anodes.

4. Conclusions

The electrochemical characteristics of the various carbon materials (graphite and hard carbon) have been evaluated for use as a negative electrode for Li-ion capacitors. Rate capability and cycle performance of the materials were compared using half and full cell configurations, respectively. The hard carbon material showed the best rate capability of about 70% retention (40C/0.2C in full cells with activated carbon cathode) and cycle life performance of about 83% retention after 10,000 cycles. For Li-ion capacitors, hard carbon is more suitable in terms of rate capability and cycle performance, which are core requirements of high power applications.

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