CARBON MATERIALS FOR HIGH POWER NEGATIVE ELECTRODES OF LITHIUM-ION BATTERIES AND CAPACITORS

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Some grades of graphite/carbon materials were investigated as high power negative materials for negative electrodes of lithium-ion batteries and lithium-ion capacitors. It was shown that such types of hard carbon, like CARBOTRON P from petroleum pitch (the Kureha Corporation) may be an especially interesting material for realization of lithium-ion capacitor. The main advantages of such a material are the possibility to use low cost electrolytes based on propylene carbonate as well as fast rechargeable performance. Nevertheless, such hard carbon has an irreversible capacity (ca 25%), which is somewhat higher than for typical graphite materials (ca 10-15%). It should be noted that the negative electrodes with CARBOTRON P also have to contain ca 3% w/w of Timcal Super C65 conductive carbon black as a carbon percolator in order to achieve a high capacity of 240 mA·h/g at 5C discharge rate.

Recently, a wide variety of carbon types have been used in negative electrodes [1]. Some cells utilize graphite materials available at a relatively low cost, while others utilize some hard carbons that demonstrate capacities higher than those of graphite materials. Previously, it was suggested that hard carbon (HC) has some disadvantages in comparison with graphite: (i) HC has a very poor rate performance related to a slow diffusion of lithium in the internal carbon structure; (ii) the HC charge/discharge curve is not flat, and the potential gradually varies during the deintercalation/intercalation process; (iii) HC has a large initial irreversible capacity. Graphite-based electrodes do not have the above-mentioned disadvantages, and therefore they are considered the best choice for the negative electrodes of lithium-ion capacitors. On the other hand, hard carbons have the advantage that they can intercalated/deintercalated in a low cost electrolyte based on propylene carbonate (PC), which has a superior conductivity at lower temperatures. Also, hard carbons show very small changes of volume during the charge/discharge. This characteristic is a benefit for prolonged cycling of the anode. Thus, hard carbon may be quite promising for the new generations of anode materials for the lithium-ion batteries (LIB) and lithium-ion capacitor (LIC). We have investigated the opportunity to improve the electrochemical performance of the anode of LIB and LIC.

Research methodology

Versatile electro-chemical testing of different anode materials was conducted in order to estimate their possible application for high power lithium-ion batteries and lithium-ion capacitors. Electrodes were composed of 90% of active material, 7% of the binder – polyvinyliden fluoride (PVDF) and 3% of carbon percolators. Slurries for electrode casting were prepared from a mixture of the graphite and PVDF dissolved in 1-methyl-2-pyrrolidinone (NMP). They were spread onto a Cu foil with different thickness and dried under vacuum at 120^{o}C for 12 h. After drying, the electrodes were compressed by roll press. The thickness of active mass after rolling was varied within a wide range from 50 µm. The density of active layer was about 1.3 g/cm^3. The 2016 type of half-elements with lithium electrode were assembled using the electrodes with an operating area of 2.0 cm^2. All these elements were assembled in the argon box (M Braun, USA) with a water content of < 1 ppm. Electrochemical investigations were performed using the multi-channel potentiostat/galvanostat VMP3 from Princeton Applied Research (UK). The electrochemical performance of materials was examined using a range of measurement techniques.

Results and Discussion

In this work, advanced carbonaceous materials were investigated in order to find the best materials for LIC and the high power LIB. For example, the Kureha Corporation developed advanced carbon products such as CARBOTRON P from petroleum pitch. CARBOTRON P is an activated anode material for the LIB, which makes excellent use of Kureha's structure control technology for carbon materials. Although CARBOTRON P is classified as non-graphitizable carbon (called "hard carbon" due to its structure), it is different from other hard carbons because of its specially designed structure, which can ensure very fast diffusion of Li-ions inside the particles. The structure of CARBOTRON P is stable and has little changes even after repeated input and output of Li ions. This is why we suggested testing this material for the LIC and the high power LIB.

The higher reversible capacity (up to 1000 mA·h/g) could be obtained for hard carbons using the lower current density and discharge with the platting of Li as described in [2]. On the other hand, this method could not be accepted in the case of LIC and LIB. Thus, we have estimated the electrochemical properties of hard carbon in the conditions, used typically for graphite testing. Figure 1 shows the voltage profiles of hard carbon at current densities of C/20 and C/2.

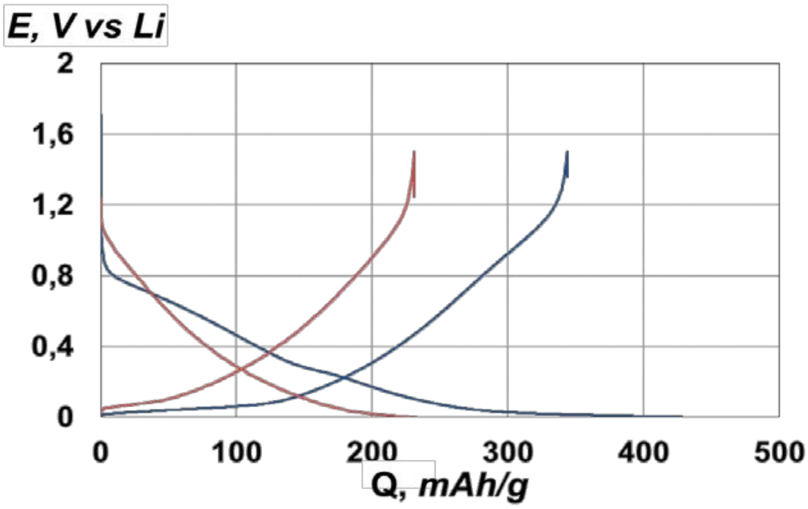

Fig. 1. Profiles of charge/discharge potentials of the hard carbon at current densities of C/20 (blue line) and C/2 (red line)

The reversible capacity of hard carbon on lithium deintercalation was seen to be 344 mA·h/g within the range of cut-off potentials from 0.0 to 2.0 V. The irreversible capacity was 84 mA·h/g, which is slightly higher than that in the case of common graphite materials for lithium-ion battery. For example, the same test was done for commercial types of graphite materials such as MCMB (MesoCarbon MicroBeads) obtained from MTI Corporation. The reversible capacity of MCMB (TB-17) at the first cycle was of 349 mA·h/g. Irreversible loss of capacity at the first cycle came to 25 mA·h/g. It is necessary to note that irreversible capacity is correlated to the surface area of material. MCMB has a lower specific surface area than CARBOTRON P, thus a lower irreversible capacity.

In order to select the best anode materials for LIB and LIC, we performed long-term tests in order to study the stability of carbon materials at the C/5 discharge rate. The results are shown in Fig.2 and 3.

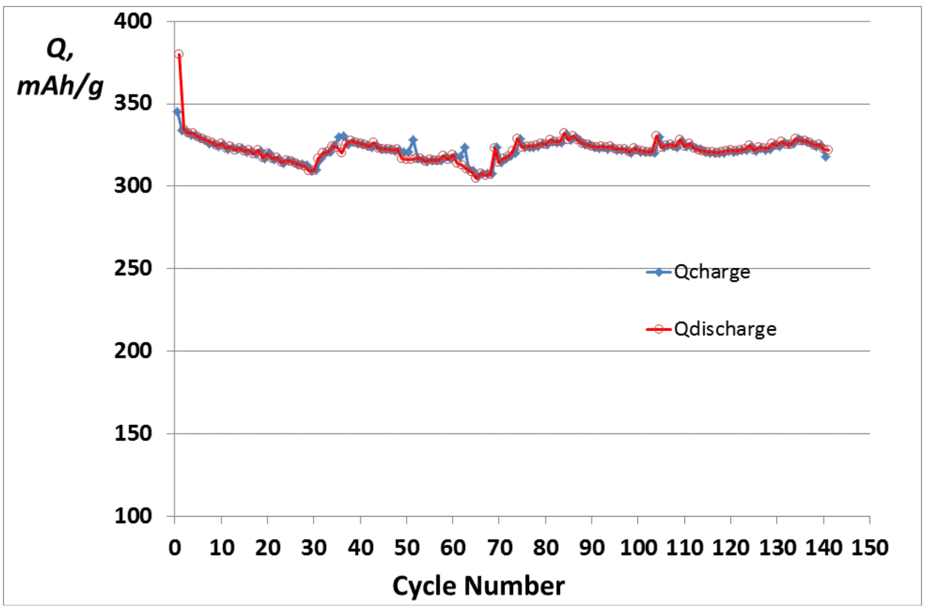

Fig. 2. Cycling performance of MCMB (TB-17) at C/5 discharge rate

According to Fig. 2 after ca 50 cycles discharge capacity of graphite material, such as MCMB was at the level of Q ~ 322 mA·h/g. This result indicates that the electrode has a quite good cyclic stability in such test conditions. Nevertheless, some fading of capacity with cycling was observed at initial stage of test.

Fig.3 presents the cycle ability of electrode based on CARBOTRON P. This material shows superior cycling stability. Thus, hard carbon CARBOTRON P may be especially interesting materials for LIC realization.

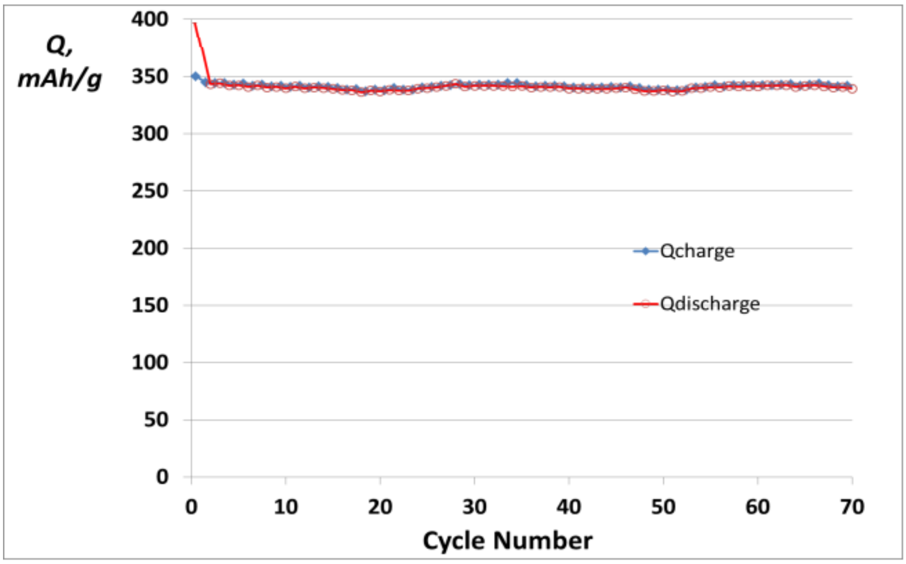

Fig. 3. Cycling performance of hard carbon (CARBOTRON P) at C/5 discharge rate

It is well known that the reversible specific capacity of anode materials decreases with increasing the current rate. Despite that, a fast rechargeable performance is one of the most important properties required for LIC and the high power LIB. In this work, hard carbon and MCMB have been studied at various current densities in the half-cells using a Li metal counter electrode. Figures 4 and 5 shows discharge capability of anode materials obtained as a function of discharge rate. Discharge capability was determined at different C-rates with a charge of C/5 in the voltage range: 0.001-1.50 V vs. Li. MCMB shows (Fig. 4) a moderate performance in the fast charge/discharge test. For example, the MCMB anode shows decay in the specific capacity to ca 200 mA/g at 5C rate and ca 20 mA/g at 12.5C rate (see Figure 3, discharge current 20 mA and 50 mA).

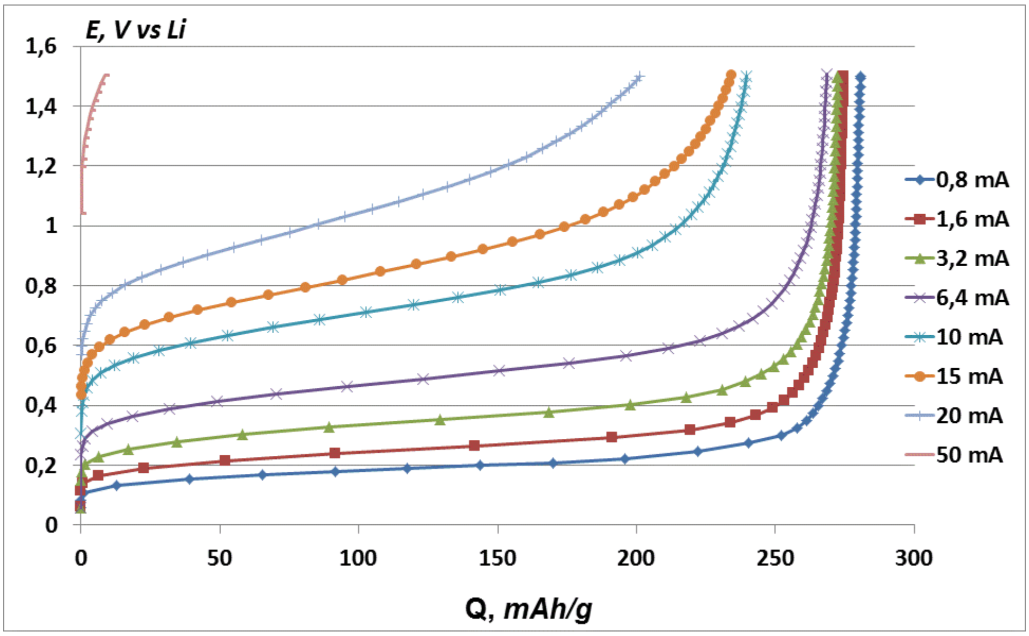

Fig. 4. Discharge capability of MCMB (TB-17) at different C-rate with a charge of C/5 in the voltage range 0.001-1.50 V vs. Li

Hard carbon (CARBOTRON P) shows better power performance than synthetic graphite such as MCMB (TB-17). For example, hard carbon anode showed very impressive anodic performance at high discharge rate (see Figure 5). Thus, CARBOTRON P shows decay in the specific capacity up to ca 240 mA/g at 5C rate and ca 80 mA/g at 25C rate (see Figure 5, discharge current 20 mA and 100 mA). This level of anodic performance at high discharge rate is thought to be possible due to unique carbon structure of CARBOTRON P.

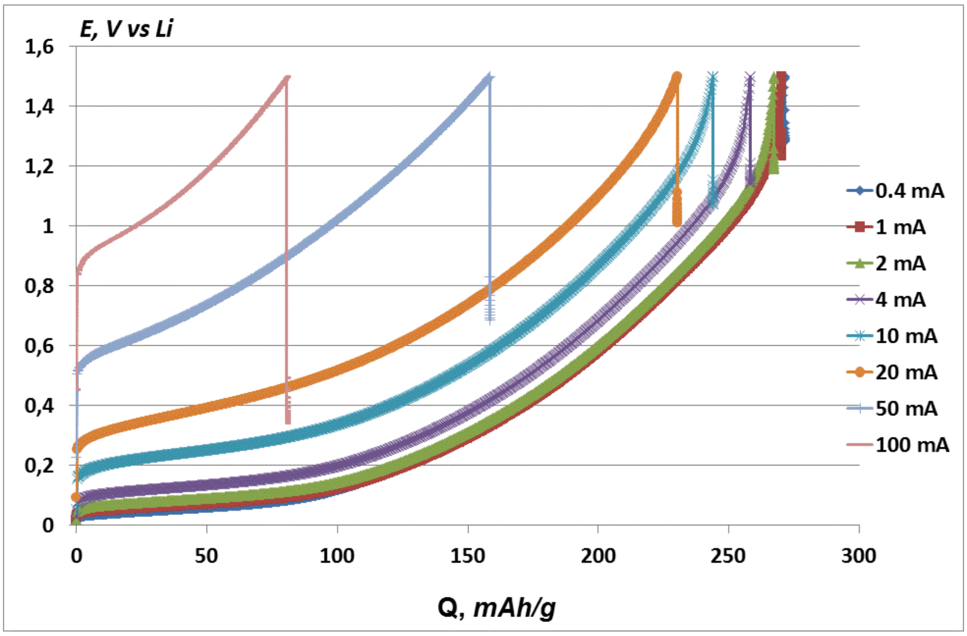

Fig. 5. Discharge capability of Hard Carbon at different C-rates with a charge of C/5 in the voltage range 0.001-1.50 V vs. Li

Nevertheless, in order to achieve good anode performance with fast discharge rate, additional technical approaches have been proposed. The method is connected with the enhancement of electron transportation kinetics and the achievement of high ionic conductivity in the electrode. It should be noted that all above-mentioned electrodes contained 3% w/w Timcal Super C65 conductive carbon black. It was found that the graphite anode without such a carbon percolator could not deliver a capacity of ca 200 mA·h/g at 2C discharge rate.

The composite electrodes based on CARBOTRON P with a carbon percolator such as C65 are very promising in terms of electrochemical performance. These electrodes certainly deserve further investigations and optimization efforts.

Conclusions

In order to continue improving the performance of state-of-the-art lithium-ion batteries and lithium-ion capacitors, some novel anode materials are required. In this work two types of carbonaceous materials were tested. We have concluded that the hard carbon (such as CARBOTRON P) and the synthetic graphite (MCMB, TB-17) show good perspective to high power performance. The effect of one manufacturing parameter such as the carbon percolator was experimentally investigated as well. Negative electrodes of LIBs and LICs with the carbon percolator (Timcal Super C65 conductive carbon black) show a higher discharge capacity at higher current rates (over 2C). Cells with the hard carbon such as CARBOTRON P show clearly a better performance. We would like to stress that this effect is due to the unique carbon structure of CARBOTRON P.

Acknowledgement

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