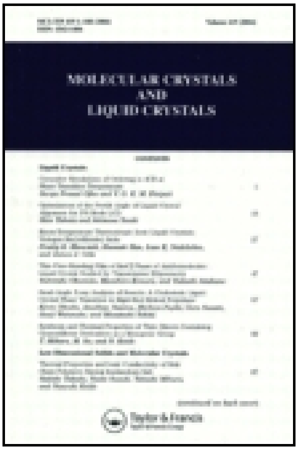
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Overview of Carbonaceous Materials for Lithium Ion Battery

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OVERVIEW OF CARBONACEOUS MATERIALS FOR LITHIUM ION BATTERY

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The relationship between gravimetric and volumetric capacities of carbonaceous materials used for a negative electrode of a lithium ion battery is discussed.

Keywords: gravimetric capacity; volumetric capacity; lithium ion battery

INTRODUCTION

After lithium ion battery was commercialized, it passed exactly for ten years. Progress in carbonaceous materials for a negative electrode is surprisingly remarkable.

Figure 1 shows the change of the capacity improvement of a cylindrical lithium ion battery 18650 after the commercialization. Mainly this capacity improvement is based on the improvement of carbonaceous materials for a negative electrode. Four kinds of carbonaceous materials, 1) graphite, 2) soft carbon, 3) hard carbon and 4) low temperature treated carbon, have been proposed for lithium ion battery. Each carbonaceous material has different characteristics such as charge-discharge curve and capacity. Up to now, the exact mechanism of lithium ion absorption is not yet clarified. Consideration of the maximum value of lithium ion absorption into these carbon materials suggests an important key to speculate the lithium ion absorption mechanism.

DISCUSSION

It seems reasonable to argue the maximum value of lithium ion absorption based on gravimetric capacity (mAh/g) of carbonaceous materials, but volumetric capacity (mAh/cm^3) is more suggestive to consider the

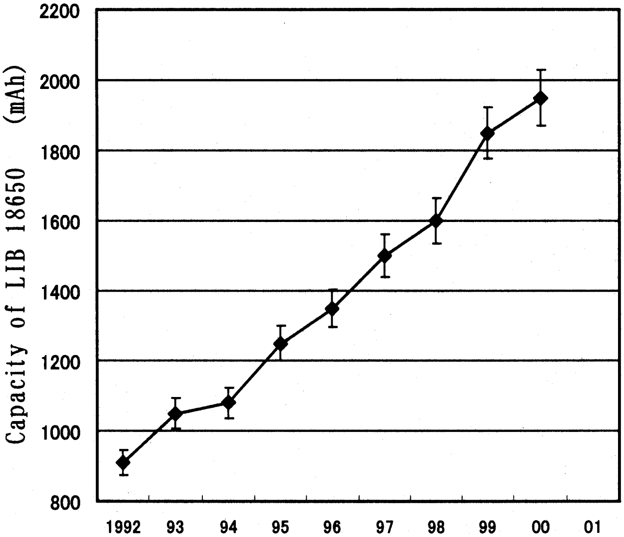

FIGURE 1 Improvement of cell capacity of lithium ion battery (LIB).

mechanism. It is necessary to measure the real density of lithium ion absorbed carbonaceous materials to obtain the volumetrical capacity value. The real density values at discharged state and charged state of three kinds of carbonaceous materials, graphite, and hard carbon and low temp. carbon, are shown in Table 1.

Reversible charge-discharge capacities of these materials are measured using 1 M $LiPF_6$ electrolyte dissolved in ethylenecarbonate/ethylmethylcarbonate (1:2) mixed solvent. The gravimetric capacity is calculated based on the weight of carbonaceous materials and absorbed lithium. The

TABLE 1 The Relationship of Gravimetric and Volumetric Capacity of Various Carbonaceous Materials

Carbonaceous materials	Graphite	Hard carbon	Low temp. carbon
Real density (g/cm^3) at discharged state	2.25	1.6	1.8
Real density (g/cm^3) at charged state	2.1	1.6	1.8
Gravimetric capacity (mAh/g)	347	490	767
Volumetric capacity (mAh/cm^3)	780	799	1380

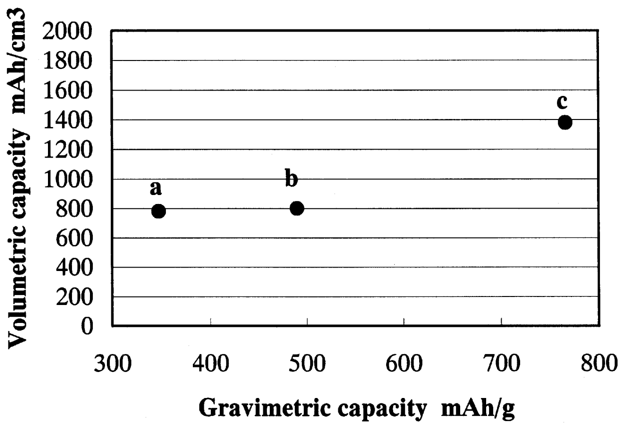

FIGURE 2 Gravimetric and volumetric capacity of various carbonaceous materials. a: graphite, b: hard carbon, c: low temp. carbon.

volumetric capacity is calculated based on the real density of carbonaceous materials at charged state. The values of gravimetric capacity and volumetric capacity are shown in Table 1 and Figure 2.

Hard carbon has much higher gravimetric capacity than graphite, but volumetric capacity is almost the same, suggesting that both hard carbon and graphite absorbs the same number of lithium species in unit volume. Ionic repulsion of lithium species in carbonaceous materials is one of the factors that determine the maximum value of volumetric capacity. This result shows that the electronic or ionic state of lithium species both in hard carbon and graphite is almost the same.

On the other hand, low temp. carbon has much higher gravimetric capacity and volumetric than other two carbons. This means that low temp. carbon absorbs much more lithium species than other two in unit volume. The shorter average ionic distance of Li species in low temp. carbon calculated from Table 2 suggests that ionic repulsion of lithium species in low temp. carbon is weaker than that in other two. The electronic or ionic state of lithium species in low temp. carbon is reasonably supposed to be different from that in other two.

The relationship of gravimetric and volumetric capacities of carbonaceous materials is very suggestive to consider the mechanism of absorbing lithium species.

Similar phenomena are observed in other materials for a negative electrode such as lithium metal and lithium alloys. The real density values at discharged state and charged state of lithium metal and various lithium alloys are shown in Table 2.

TABLE 2 The Relationship of Gravimetric and Volumetric Capacities of Li or Various Li Alloys

Metal or alloys	Li	LiAl	$Li_{21}Si_5$	Li_3As	$Li_{21}Sn_5$	Li_3Sb	$Li_{22}Pb_5$
Real density (g/cm^3) at discharged state	–	2.7	2.3	5.7	7.3	6.7	11.4
Real density (g/cm^3) at charged state	0.534	1.7	1.15	2.4	2.6	3.1	3.8
Gravimetric capacity (mAh/g)	3884	791	1978	838	760	563	495
Volumetric capacity (mAh/cm^3)	2075	1364	2272	2012	1953	1768	1873

Here, the gravimetric capacity is calculated based on the theoretical values, and the volumetric capacity is calculated based on the real density of lithium metal or alloys at charged state. The values of gravimetric and volumetric capacities are shown in Table 2 and Figure 3. Lithium metal and alloys have different gravimetric capacity values, but volumetric capacity values are very similar. This means that both lithium metal and various lithium alloys absorb the same number of lithium species in unit volume. This result suggests that the electronic or ionic state of lithium species in lithium metal and various lithium alloys are similar and repulsion of lithium species in these materials is almost the same.

It is very interesting that the maximum volumetric capacity value of low temp. carbon is close to those of lithium metal and alloys. This result

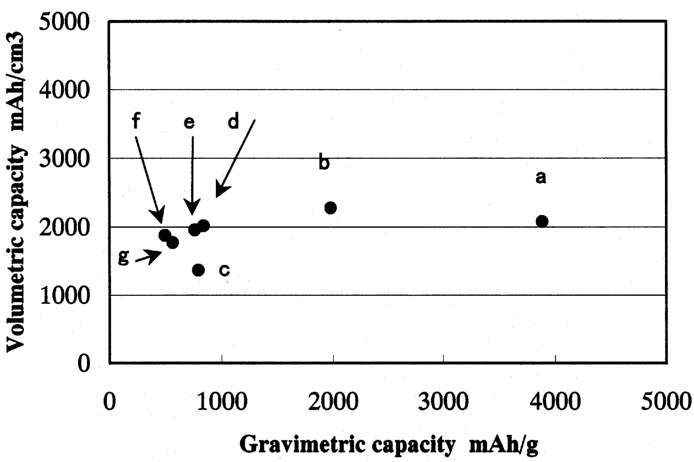

FIGURE 3 Gravimetric and volumetric capacities of Li or various Li alloys. a: Li, b: LiAl, c: $Li_{21}Si_5$, d: Li_3As, e: $Li_{21}Sn_5$, f: Li_3Sb, g: $Li_{22}Pb_5$.

suggests that the electronic or ionic state of lithium species in low temp. carbon is similar to that in lithium metal and alloys.

SUMMARY

The relationship between gravimetric and volumetric capacities of carbonaceous materials and other materials used for a negative electrode of a lithium ion battery is discussed.

Volumetric capacity is very suggestive to speculate the electronic or ionic state of lithium species in lithium absorbing materials.