



Large discharge capacity from carbon electrodes in sulfuric acid with oxidant

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Abstract

The discharge performance of the graphite intercalation compounds in sulfuric acid containing nitric acid (H_2SO_4 -GICs) was studied by focusing on the effects of oxidant and carbon nanotexture. A large discharge capacity from H_2SO_4 -GICs synthesized by using an excess amount of HNO_3 , more than 150 times of the theoretical value (93 mAh/g carbon), was obtained depending on the amount of oxidant added, the discharge current, and the nanotexture of carbon electrode. The experimental results are explained in terms of competition between the de-intercalation of sulfuric acid due to galvanostatic reduction and the re-intercalation due to chemical oxidation by HNO_3 during discharging. However, a subsidiary reaction decreases the effective amount of HNO_3 on the discharge by a small current and also on the cycle of chemical charging and electrochemical discharging. The oxidant $KMnO_4$ gave only a little larger capacity for discharge than the theoretical one, because it was reduced to the manganese oxide precipitates during the oxidation of the carbon electrode.

Keywords Graphite intercalation compounds; Discharge behaviour; Sulfuric acid, Chemical oxidation; Texture

1. Introduction

The formation of graphite intercalation compounds (GICs) with sulfuric acid has been studied by a number of authors by means of either chemical or electrochemical processes [1–4]. The H_2SO_4 -GICs synthesized through chemical oxidation has been widely used as a precursor for preparing exfoliated graphite. Intercalation and de-intercalation of sulfuric acid into graphite gallery by electrochemical methods have been proposed to be used as electrode reactions for a battery [5,6].

Recently, we followed the chemical oxidation of graphite, resulting in the intercalation of sulfuric acid into graphite, by measuring the potential of the electrode, and we showed that the formation process of H_2SO_4 -GICs by chemical oxidation is exactly the same as that by electrochemical oxidation [7]. The potential changes with chemical oxidation was quantitatively explained by referring to the potential curves with galvanostatic oxidation which had been discussed in detail in Ref. [8]. The criteria for the intercalation of sulfuric acid were clarified from the viewpoints of the intercalate, amount of oxidant, concentration of H_2SO_4 , and host carbons [9]. From these results, the oxidation by the

chemical method is shown to correspond to the charging process from the viewpoint of electrochemistry. This suggested to us to work on chemical charging and electrochemical discharging through the formation and decomposition of H_2SO_4 -GICs [10]. It was possible to obtain a large discharge capacity in sulfuric acid containing a certain amount of nitric acid, and it was shown to be mainly due to the competition between the intercalation of H_2SO_4 by chemical oxidation and the de-intercalation by electrochemical discharging.

In the present paper, the discharge performance of carbon electrodes was studied by focusing on the effect of the oxidant and also of the nanotexture of the carbon electrode.

2. Experimental

The cell used for the measurements of potential change during chemical oxidation and of galvanostatic reduction is shown schematically in Fig. 1(a). In the working electrode, the carbon material of 50 mg was held in between plastic plates, the details of which are illustrated in Fig. 1(b). A platinum plate was used as the counter electrode. The electrolyte is sulfuric acid with a concentration of 18 M, containing either

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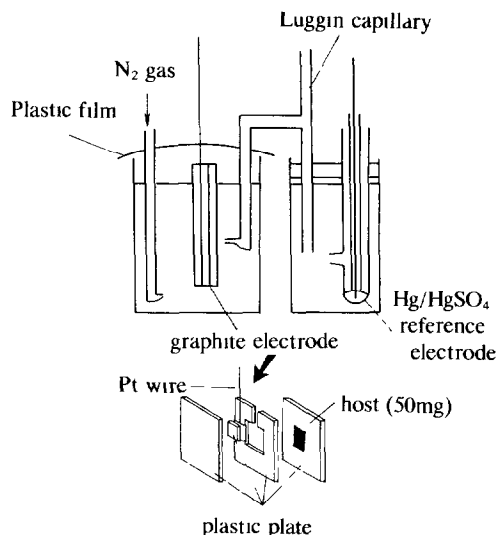


Fig. 1. Setup of the experimental cell

13.8 M nitric acid or potassium permanganate powder as the oxidant. The different molar ratios of oxidant to carbon electrode were selected. The electrolyte was kept at a constant temperature of 25 °C during the whole experiment, charging by chemical oxidation and galvanostatic reduction. The test cell was covered with a plastic film to prevent absorption of moisture from the air. The electrolyte was mixed by magnetic stirring and by nitrogen gas bubbling. The detailed experimental setup and procedure were described in our previous work, see Ref. [7].

The potential of the carbon electrode during both processes of chemical oxidation and galvanostatic reduction was measured versus a Hg/HgSO₄ electrode. Galvanostatic reduction, i.e., electrochemical discharge, from the cell was carried out by a constant current of either 0.4 or 4 mA.

Carbon materials for the electrode, i.e., hosts for the intercalation of sulfuric acid, were selected from those with different nanotextures. They are shown in Table 1, with their sample codes, employed in the present paper, and some structural parameters measured by X-ray diffraction [11]. The natural graphite powder with the average flake size of 400 μm (NG-400) and the pyrolytic carbon heat-treated at 3000 °C (PyC) have a high degree of orientation of hexagonal carbon layers along the plane (plane orientation). The mesophase-pitch-based and vapour-grown carbon fibres (MPCF-R and OVCF, respectively) with fibre diameter of 8 to 13 μm, both being heat-treated up to 3000 °C, have axial orientation of hexagonal carbon layers along the fibre axis. In their cross sections, however, the former has the radial arrangement of layers with open wedge, but the latter the concentric arrangement, as shown in Fig. 2(a) and (b), respectively. These host materials have different structural parameters, degree of graphitization P_1 , average interlayer spacing d_{002} , crystallite

sizes along the *c*- and *a*-axes, L_c and L_a . It can be said that each of them has the highest graphitization state in each nanotexture.

3. Results

3.1. Electrochemical discharging from carbon electrode

In Fig. 3, the curves of potential versus discharge capacity by galvanostatic reduction with a current of 0.4 mA are compared on the H₂SO₄-GICs synthesized from natural graphite (NG-400) through three different oxidation paths: (i) galvanostatic with a constant current of 0.4 mA; (ii) chemical by KMnO₄, and (iii) chemical by nitric acid in sulfuric acid. In the last two oxidation paths, a large excess amount of oxidant was used, the mole ratio of the oxidant to carbon being 3.3, and so a certain amount of oxidant remained in sulfuric acid electrolyte during the following galvanostatic reduction.

In Fig. 3(a), the potential changes during reduction on two GICs synthesized by galvanostatic and KMnO₄ oxidation show a distinct plateau at about 0.75 V and a faint one starting from about 0.45 V, the former is known to be due to the transformation from stage-1 to stage-2 structures and the latter can be attributed to the gradual decomposition of the stage-3 to higher stage compounds. The potential plateau corresponding to the transformation from the stage-2 to stage-3 structures is not seen on the potential change, though it has been observed on the potential changes during both galvanostatic and chemical oxidation paths [7]. The electric quantity discharged during the potential decrease down to 0.2 V, which is a rest potential for the original graphite electrode; for the GIC synthesized by galvanostatic oxidation it is about 80 mAh/g carbon, but that for the GIC synthesized by the KMnO₄ oxidation is about 130 mAh/g carbon. The theoretical quantity for the formation of the stage-1 H₂SO₄-GIC was reported to be 93 mAh/g carbon [12].

The GIC synthesized by HNO₃ oxidation, on the other hand, shows quite different behaviour during galvanostatic reduction with a current of 0.4 mA and discharges a very large electric quantity, as shown in Fig. 3(b). This is the reason why we have to show the result in a separate figure. The electric quantity for the complete decomposition (i.e., de-intercalation) reaches 14 000 mAh/g carbon, which is about 150 times of the theoretical value. It is clear that this large discharge capacity is due to the fact that the potential is held at around 0.8 V, showing even a gradual increase in potential, which roughly corresponds to the potential for the transformation of the stage-1 to stage-2 structures.

Table 1
Host carbon materials for the intercalation of sulfuric acid

Sample code	Carbon material	Heat treatment (°C)	Structure parameters			
			P_1	d_{002} (nm)	L_c (004) (nm)	L_a (nm)
NG-400	Natural graphite, flake size of 400 μm		1.00	0.3354	360	> 1000
PyC	Pyrolytic carbon	3000	0.71	0.3359	120	> 1000
MPCF-R	Mesophase-pitch-based carbon fibres	3000	0.52	0.3368	29	86
OVCF	Vapour-grown carbon fibres	3000	0.80	0.3360	115	160

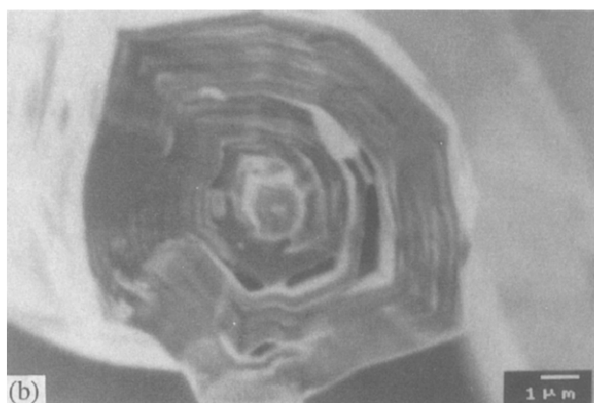
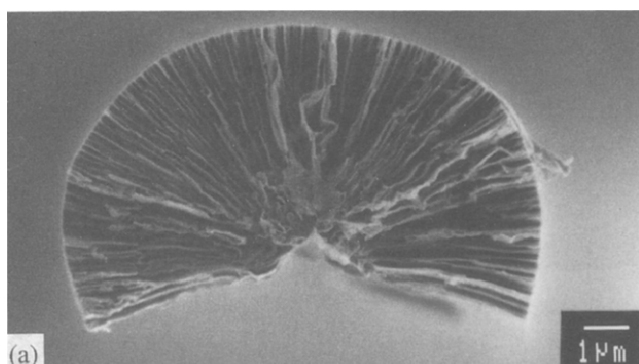


Fig. 2 Scanning electron micrographs of the (a) mesophase-pitch-based carbon fibre (MPCF-R) and (b) vapour-grown carbon fibre (OVCF) heat-treated at 3000 °C.

3.2. Repetition of electrochemical discharging

After the galvanostatic reduction down to the potential 0.0 V with a current of 0.4 mA (Fig. 3(b)), i.e., complete decomposition of the GIC synthesized by HNO_3 oxidation, the potential of the graphite electrode was found to increase spontaneously by opening the circuit. So, the potential changes during the repetition of these spontaneous chemical oxidation and galva-

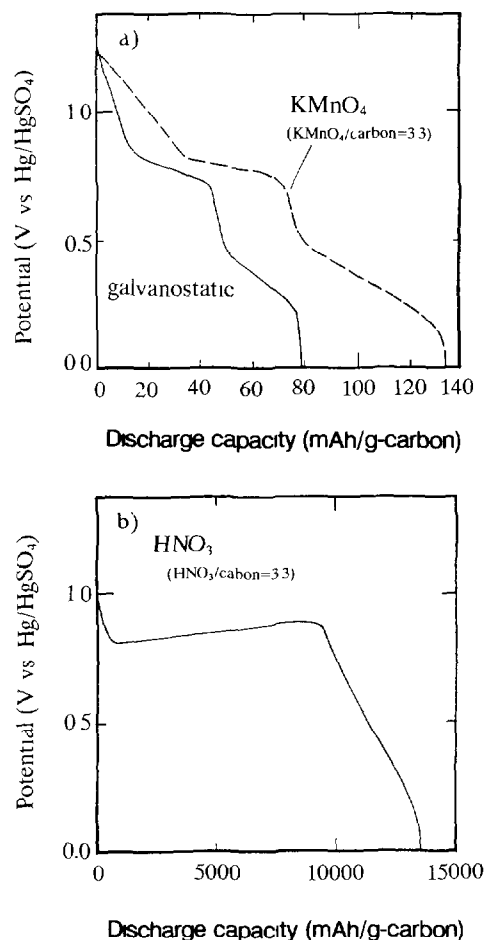


Fig. 3. Potential changes of the electrode of natural graphite (NG-400) during galvanostatic reduction: (a) prepared by galvanostatic oxidation and by KMnO_4 oxidation, and (b) by HNO_3 oxidation.

nostatic reduction were followed by using the ratio of HNO_3 /carbon=3.3 at the start and the electrode of NG-400. In Fig. 4, the results are shown by plotting the potential versus time during the oxidation and versus the electric quantity during galvanostatic reduction with the current of 0.4 mA. When the potential

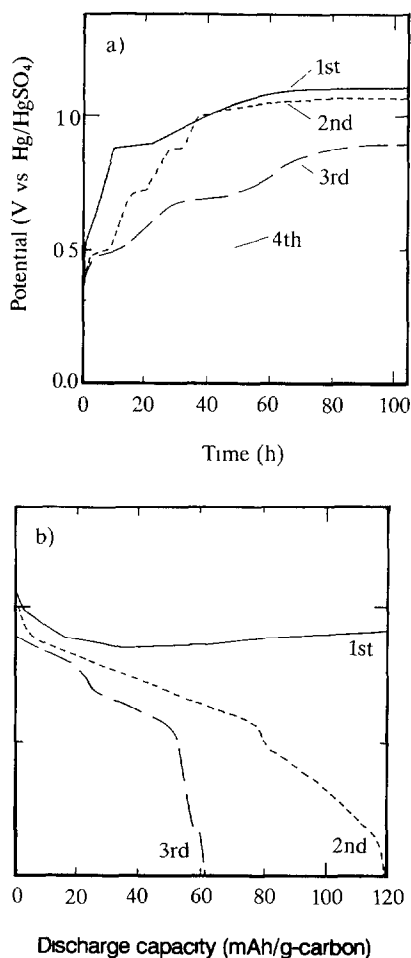


Fig. 4. Charge and discharge behaviours vs. cycle: (a) the charge was performed by HNO_3 oxidation, and (b) the discharge by galvanostatic reduction with 0.4 mA. The starting ratio of $\text{HNO}_3/\text{carbon}=3.3$, and the electrode was NG-400.

reaches at 0.0 V by galvanostatic reduction (Fig. 4(b)), the curve returns to the time zero on the left-hand side in Fig. 4(a). The first reduction discharged such a large electric quantity, as Fig. 3(b), that only the beginning of potential change was shown in the figure.

After the first reduction down to the potential 0.0 V (not shown in Fig. 4(b)), the potential of the electrode increases spontaneously showing distinct plateaus corresponding to the stage transformations and finally reaches the saturated potential of 1.05 V (Fig. 4(a)), the curve '2nd', almost the same value as in the first oxidation. The GIC formed by this second oxidation cycle has a stage-1 structure. The discharge capacity after this second oxidation greatly decreases, less than one hundredth of that of the first reduction. After this second reduction cycle, the potential of the graphite electrode increases spontaneously by opening the circuit, but it saturates at 0.8 V (the curve '3rd'). The GIC formed in this stage had a stage-2 structure. The discharge capacity during the third reduction cycle decreases to about 65 mAh/g carbon. After the third

galvanostatic reduction cycle, the increase in potential by opening the circuit is slow and saturated below 0.5 V (the curve '4th').

When HNO_3 in the amount of $\text{HNO}_3/\text{carbon}=3.3$ was added again into this electrolyte after finishing the 4th galvanostatic reduction cycle, the same potential curves as the first oxidation and reduction in Fig. 4 were found to be recovered, spontaneous stepwise increase in potential during chemical oxidation and large discharge capacity during galvanostatic reduction.

The behaviour of galvanostatic reduction was found to depend also on the discharge current. In Fig. 5, the potential changes during the repetition of chemical oxidation and galvanostatic reduction with the current of 4 mA, ten times larger than that in the experiments shown in Figs. 3 and 4, are shown on the electrode NG-400. The discharge capacity in every cycle of galvanostatic reduction is about 120 mAh/g carbon, much smaller than that observed in the first cycle with the current of 0.4 mA. However, no change in the potential curves during chemical oxidation and galvanostatic reduction were observed even after the 21st cycle.

Using KMnO_4 as oxidant, no spontaneous oxidation by opening the circuit was observed after the first galvanostatic reduction.

3.3. Effect of amount of HNO_3 on discharge performance

The discharge performance during galvanostatic reduction depends also on the amount of HNO_3 added at the start of chemical oxidation. The potential changes with electric quantity during galvanostatic reduction are shown in Fig. 6 on the GICs synthesized from the sample NG-400 by chemical oxidation using different amounts of HNO_3 ($\text{HNO}_3/\text{carbon}=3.3, 6.6$ and 16.6). All of these amounts of HNO_3 are in large excess for the formation of the H_2SO_4 -GIC with stage-1 structure and, as a consequence, a certain amount of HNO_3 remains even after reaching the saturated potential, i.e., finishing the chemical oxidation or charging. The current for the galvanostatic reduction was 4 mA, because the reduction with 0.4 mA needs such a long time to finish the de-intercalation.

The discharge capacity increases with the increasing amount of HNO_3 added. For $\text{HNO}_3/\text{carbon}=3.3$ it is about 140 mAh/g carbon by 4 mA discharging, though it reaches 14 000 mAh/g carbon by 0.4 mA discharging, as shown in Fig. 3(b). For $\text{HNO}_3/\text{carbon}=16.6$, however, the discharge with the electric current of 4 mA was continued even after three months, which could not be shown in Fig. 6. The large discharge capacity is caused by a very slow decrease in potential, particularly around 0.8 and 0.45. In the case of $\text{HNO}_3/\text{carbon}=6.6$, the potential looks like to be saturated at about 0.25 V.

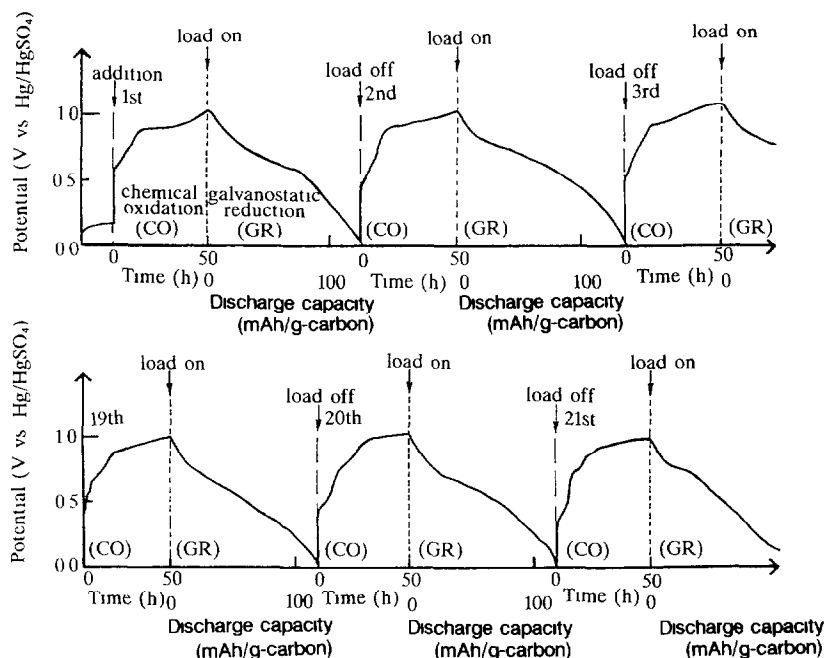


Fig. 5. Potential changes during the repetition of HNO_3 oxidation and galvanostatic reduction with a current of 4 mA on the electrode NG-400

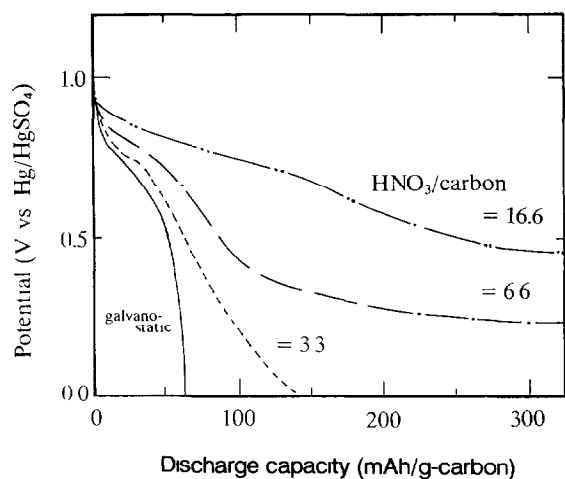


Fig. 6. Effect of the amount of HNO_3 ($\text{HNO}_3/\text{carbon}$) on the discharge performance with the current of 4 mA on the electrode NG-400

3.4. Effect of carbon materials on discharge performance

The effect of the nanotexture of carbon materials for the discharge performance in H_2SO_4 electrolyte containing a certain amount of HNO_3 was studied by using four carbon materials shown in Table 1.

In Fig. 7, the potential changes during galvanostatic reduction after getting the saturated potential of 1.05 V by the chemical oxidation with HNO_3 are compared on four host materials. The ratio of $\text{HNO}_3/\text{carbon}$ was fixed at 3.3 and the discharge current at 4 mA.

The discharging behaviour depends strongly on the nanotexture; using the hosts with plane orientation the discharge capacity of about 150 mAh/g carbon is ob-

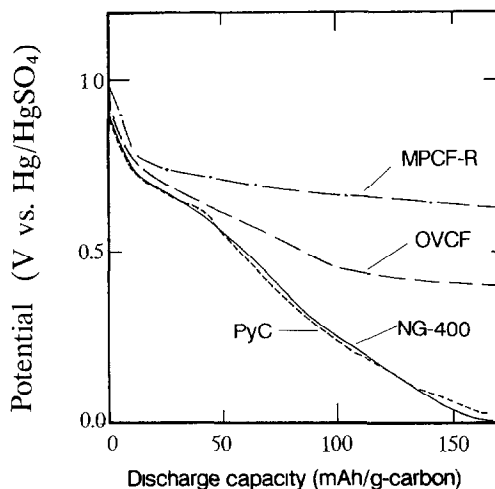


Fig. 7. Potential changes during galvanostatic reduction with a current of 4 mA on the electrode of different carbon materials shown in Table 1.

tained, but the hosts with axial orientation give more than 500 mAh/g carbon, much higher than the theoretical capacity. The mesophase-pitch-based carbon fibres with radial arrangement in their cross sections, MPCF-R, showed a discharge capacity of more than 15 000 mAh/g carbon [10]. The electric quantity up to 10 000 mAh/g carbon is obtained at a rather constant voltage of 0.7 V.

In Fig. 8(a) and (b), the scanning electron micrographs of MPCF-R and OVCF, respectively, after discharge are shown. The fibres are broken, reasonably supposed to occur during the oxidation, i.e., intercalation of sulfuric acid.

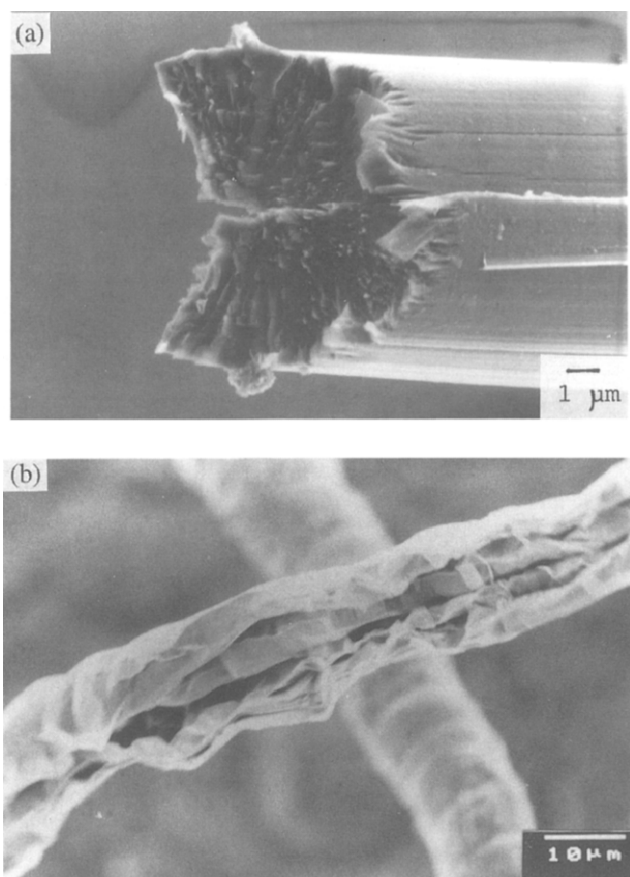


Fig. 8 Scanning electron micrographs of the electrodes MPCF-R and OVCF after discharging (a) mesophase-pitch-based carbon fibre (MPCF-R), and (b) vapour-grown carbon fibre (OVCF)

4. Discussion

The intercalation of sulfuric acid into the graphite gallery by chemical oxidation was found to be associated with a stepwise potential increase due to the extraction of carrier electrons from the host carbon layers [8]. The existence of carrier electrons in the conduction band of the host carbon materials was shown to be one of the criteria for the intercalation of sulfuric acid [9]. At the same time as the oxidation of carbon layers of the hosts, the oxidant molecules themselves were reduced by the electrons extracted from the hosts. The chemical reactions on the oxidants HNO_3 and KMnO_4 are expressed as follows:



In the case of HNO_3 , the reduction product HNO_2 is soluble in sulfuric acid and it can therefore be oxidized to NO_3^- , probably on the platinum counter electrode during the reduction of carbon electrode. In other words, the reaction Eq. (1) can be a reversible one in the present experimental setup. The oxidant KMnO_4 ,

on the other hand, gives precipitates as the reduction product and so the reaction (Eq. (2)) can not be reversible. The chemical composition of the precipitates has been estimated to be MnO_3 though they are usually in an amorphous state [7].

For galvanostatic reduction, i.e., de-intercalation, of H_2SO_4 -GIC synthesized by using an excess amount of HNO_3 , a large electric quantity was obtained, more than 150 times of the theoretically expected one. The electric quantity for the de-intercalation, i.e., discharge capacity, decreased with the increase in reducing current from 0.4 to 4 mA, in other words, with the increase in reaction rate of the de-intercalation. With the increase in amount of HNO_3 added, the discharge capacity increased. These experimental results reveal the occurrence of two reaction competitive processes; the galvanostatic reduction of H_2SO_4 -GIC, and the chemical oxidation (re-oxidation) to H_2SO_4 -GIC by the oxidant HNO_3 . The rate of galvanostatic reduction is controlled by the current, as mentioned above. The rate of chemical oxidation is reasonably supposed to be governed by the amount of the oxidant HNO_3 in the electrolyte solution. When the discharge current was as small as 0.4 mA and the excess amount of HNO_3 ($\text{HNO}_3/\text{carbon}=3.3$) was added, the re-oxidation seems to be a little superior to the galvanostatic reduction and so the potential increase was observed even during discharge, which resulted in a large discharge capacity. With the discharge current of 4 mA, the reduction rate overcome the re-oxidation rate and a consequently smaller discharge capacity was obtained. By increasing the amount of HNO_3 added in the beginning, the amount of HNO_3 remained in sulfuric acid solution after the first oxidation cycle increased and the oxidation rate became competitive with the reduction rate, resulting in a very slow decrease of potential during galvanostatic reduction and in a large discharge capacity.

During the reduction of HNO_3 in sulfuric acid, associated with the chemical oxidation of host carbon to H_2SO_4 -GICs, we have to postulate a subsidiary reaction, in addition to the reaction expressed by Eq. (1). Through the subsidiary reaction, the oxidant HNO_3 seems to be changed to something out of the reaction system, though any precipitation and gas formation were not detected during chemical oxidation of host carbon, and, as a consequence, the effective amount of oxidant decreased gradually. When the discharge current was 0.4 mA and the galvanostatic reduction was going slowly, the subsidiary reaction seemed to proceed and to give a large loss of the oxidant. This was the reason why the potential started to decrease after the discharge of a certain quantity of electricity (Fig. 3(b)). With the discharge current of 4 mA, less amount of the oxidant was lost and, therefore, many cycles of galvanostatic reduction and chemical oxidation were possible (Fig. 5).

It is clear from the above discussion why large discharge capacity, larger than the theoretical one, was not obtained by using KMnO_4 , and no cycle of spontaneous oxidation and electrochemical discharge was possible.

As discussed above, there is a competition between galvanostatic reduction of and chemical oxidation to H_2SO_4 -GIC during electrochemical discharge. The chemical oxidation of carbon is reasonably supposed to occur preferentially at the edge of the hexagonal carbon layers (graphite-like layers). Therefore, the nanotexture of host carbon materials is expected to give a strong influence on the competition between two reactions. We discussed shortly the effect of the nanotexture of carbon materials in our previous work, see Ref. [10].

The mesophase-pitch-based carbon fibres selected in the present work (MPCF-R) have a radial texture with an open wedge in their cross section (Fig. 2(a)). Using this fibre, a very large discharge capacity was obtained, which can be attributed to the fact that a large area of edge plane is exposed directly to the electrolyte because of its nanotexture. On the host materials with a plane orientation, the natural graphite NG-400 and the pyrolytic graphite PyC, however, the surface area due to edge planes is relatively small in comparison with that due to basal planes of carbon layers and the oxidation reaction cannot therefore compete with the rate of galvanostatic reduction, giving small discharge capacity. The vapour-grown carbon fibre VGCF is expected to give small edge surface areas like natural graphite from its concentric texture in its cross section (Fig. 2(b)), but in practice, during chemical oxidation the fibres are broken and make the edge surface accessible for the electrolyte, as shown in Fig. 8(b), resulting in a relatively large discharge capacity.

5. Conclusions

The present results give an idea for a new type of battery. Selecting the carbon electrode with suitable nanotexture, such as MPCF-R in the present work,

and using sulfuric acid electrolyte with an excess amount of nitric acid oxidant, a large discharge capacity is obtained. The capacity of this battery is governed by the amount of nitric acid added and the nanotexture of carbon electrode.

The construction of this battery seems to be very similar to the electric double-layer capacitors [13] which has been commercialized. In the case of the capacitor, we have to charge it from other power sources, such as solar batteries. In the present battery, however, its charge was performed through the chemical oxidation of carbon electrode, i.e., the intercalation of sulfuric acid into the gallery of carbon layers, which can be performed at room temperature and, therefore, it occurs spontaneously just after opening the circuit.

In order to get many cycles of charge/discharge in this battery, it is desired to suppress the subsidiary reaction which seems to loose the nitric acid. We have to study what the nature of this reaction is and how it can be stopped.

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