Short communication

# The effect of dispersion of nano-carbon on electrochemical behavior of Fe/nano-carbon composite electrode

Minato Egashira\*, Jun-ya Kushizaki, Nobuko Yoshimoto, Masayuki Morita

*Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan*

## ARTICLE INFO

## ABSTRACT

In order to estimate the effect of the dispersion of nano-carbon species into a composite electrode, ultrasonic pretreatments under various conditions have been carried out for two kinds of nano-carbons, vapor grown carbon fiber (VGCF) and acetylene black, before preparing a composite electrode with iron powder. The cyclic voltammetry behavior of the resulting Fe/nano-carbon composite electrodes is significantly influenced by the kind of nano-carbon and the pretreatment conditions in spite of as a low content of nano-carbon as 20 wt.%. The largest redox current at initial cycle is obtained for Fe/VGCF composite electrode with the 30 min pretreatment of VGCF in ethanol. The dispersion of nano-carbon verifies the apparent density of the composite, and then affects the feature of three-phase interface among the ion-conducting electrolyte, the redox reaction surface, and the electron conductor.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

The progress of nano-scale material processing has provided large impact on battery technology as well as many science and technology fields. Many studies controlling nano-scale structure of battery components are addressed on the improvements of the rate capability and the mass efficiency of batteries [1–11]. It is a reasonable approach of controlling nano-texture of battery electrode to prepare composite electrode of a certain active material and a nano-carbon, because nano-carbons are favorable for the use in electrochemical devices due to their high electronic conductivity and high stability both chemically and electrochemically.

The concern of the authors is iron electrode for the use as negative electrode of iron-air battery. Iron-air battery has been assumed as a novel candidate for electric vehicles due to its high theoretical energy density as 1200 Wh kg$^{-1}$, and has already been developed by some suppliers e.g., Swedish National Development Co. [12,13]. However, the energy density and the power density of practical cell are as low as 80 Wh kg$^{-1}$ and 40 W kg$^{-1}$ due to some problems on both positive (air) and negative electrodes for wider use of this kind of battery. On the negative electrode side, the low ratio of utilization of iron active species and its poor cycle stability are the problems to which iron electrode is responsible. The modification of both electronic and ionic conduction through the interface where the redox reactions of iron occur appears to be effective to improve the utility and the cycle stability of iron electrode. Recently an approach for this problem has been made by preparing the composite electrode of iron with various nano-carbon materials with an assistance of one of the authors [14,15]. In the report the content of nano-carbon is 50 wt.% and the reduction of the content of nano-carbon is necessary for practical application. Here, the authors aimed the reduction of the content of nano-carbon by improving the efficiency of nano-carbon, e.g., by enhancing the contact between nano-carbon and iron. Normally such nano-carbons form aggregate to several microns. In order to disperse nano-carbons from the aggregates, several methods have been proposed [16–21].

In the present study, the dispersion of nano-carbon has been controlled to optimize the nano-structure of the Fe/nano-carbon composite electrode with the reduced amount of nano-carbons. In this preliminary stage, two kinds of conventional nano-carbons, vapor grown carbon fiber (VGCF) and acetylene black among the carbon applied in the previous reports, are compared to estimate the effect of dispersion to obtain a better electrochemical response of the redox of iron. For the dispersion of nano-carbons, an ultrasonic treatment in organic media has been selected in order to achieve the dispersed state easily and to maintain chemical state of the surface of nano-carbon. Here the effect of the nano-carbon dispersion on the electrochemical behavior of iron is to be reported.

## 2. Experimental

VGCF with 200 nm-diameter (Showa Denko Co., Japan) and acetylene black were used as nano-carbon components. These

---

\* Corresponding author. Tel.: +81 836 85 9212; fax: +81 836 85 9201.
*E-mail address:* minato@yamaguchi-u.ac.jp (M. Egashira).

nano-carbons generally aggregate and form tens-micrometer secondary particles. In order to loosen such aggregates, an ultrasonic treatment was performed by the following procedure. Nano-carbons weighed into 0.025 g were dispersed into 20 ml of solvent, and then treated by ultrasound with 35 kHz during a certain period in an ultrasonic bath (US104, SND Co.). The solvent and time for the treatment are assumed as parameters to determine the degree of dispersion. After ultrasonic treatment, the resulted suspension was filtrated by a filter paper with the loading of iron particles (Wako Pure Chemical Co., Japan). After this procedure Fe/nano-carbon composite was obtained on the filter paper. The composite was mixed with polytetrafluoroethylene (PTFE) binder at the ratio of Fe:electrolyte:PTFE of 95:5:5, ground and pressed into sheet. A part of the sheet was cut into 7 mm-diameter pellet and used as working electrode. A three-electrode glass cell was assembled with platinum plate counter electrode, Ag/AgCl reference electrode, and $3\,mol\,dm^{-3}$ KOH aq. electrolyte. Cyclic voltammogram (CV) was performed for the cell using a potentiostat (Hokuto Denko Co., Japan) under such a condition as scan rate of $1\,mV\,s^{-1}$ and potential range between $-1.3$ to $-0.3\,V$ vs. Ag/AgCl. The apparent density of Fe/nano-carbon electrode pellet was measured from the weight of pellet having a certain dimension ($10\,mm \times 10\,mm \times$ ca. 1 mm). The resistance of the electrode pellet with the same dimension was measured by attaching two probes of a digital multimeter to the both sides of the pellet. The surface morphology of the composite was observed by a scanning electron microscope (SEM; VE-8800, Keyence Co., Japan). The extent of particle aggregation of VGCF was estimated by the observation of a transmission electron microscope (TEM; JEM-2010F, JEOL Co., Japan).

## 3. Results and discussion

Fig. 1 shows TEM images of VGCF without (a) or with 30 min of ultrasonic dispersion in ethanol (b). VGCF fibers with hundreds nanometer diameter are observable in both images. Without ultrasonic treatment, VGCF aggregates to secondary particle of micrometer size. Such secondary particles appear to be loosened by the ultrasonic treatment. The resulted feature is a smaller aggregate with radial branches of VGCF fibers. The impact of the ultrasonic treatment on the dispersion of VGCF is clear from the comparison of these features. Similarly, acetylene black is expected to form an aggregate as received, and to be dispersed by proper ultrasonic treatment.

Fig. 2 shows SEM images of Fe/VGCF composite electrodes containing untreated VGCF (a) and VGCF treated by ultrasound in ethanol during 30 min (b). As shown in Fig. 2(a), untreated VGCFs form aggregates with tens of micrometer and separated from iron particles. In contrast, the composite electrode containing dispersed VGCF exhibits an image where none of such aggregate and a dis-
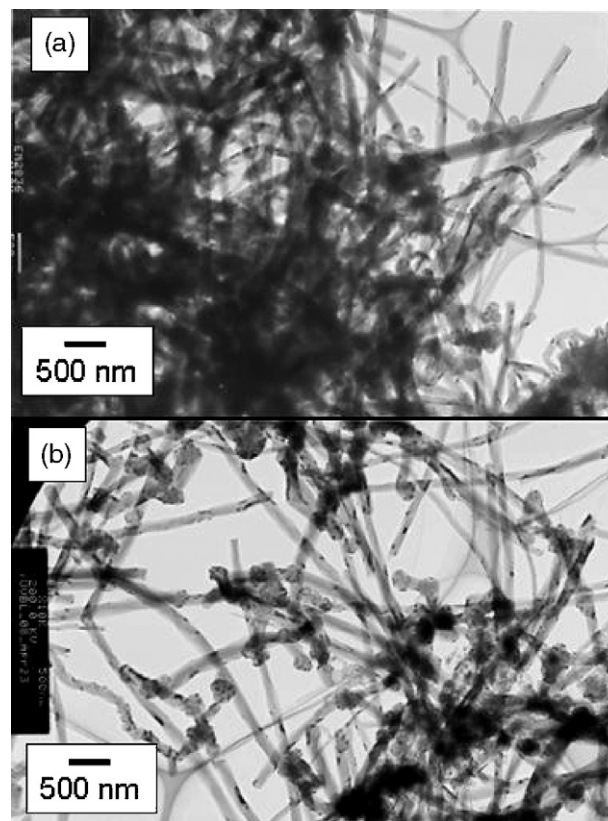


**Fig. 1.** TEM images of VGCF: (a) as-received; (b) after ultrasonic treatment at 30 min in ethanol.

persed feature of VGCF into the interparticle space of iron were obtained.

The apparent densities of composite electrode sheets with different nano-carbon components, dispersion solvents and ultrasonic treatment time were summarized in Table 1. The apparent density of the composite electrode provides a suggestion about the extent of the porosity of the electrode because the gravimetric ratio of nano-carbon, PTFE and iron is similar in all cases. That is, a composite having smaller apparent density must exhibit the larger porosity. Under such situation, one can expect that the dispersion of nano-carbon and the subsequent packing of the small portion of nano-carbon into interparticle space of iron provide the increase of the apparent density. Actually in most cases, the longer time for ultrasonic treatment provides the larger apparent density. This effect appears to be more significant for VGCF than for acetylene black. However, it should be noted that the apparent density of Fe/VGCF composite decreases by the ultrasonic treatment of

**Table 1**
Properties of Fe/nano-carbon composite electrodes

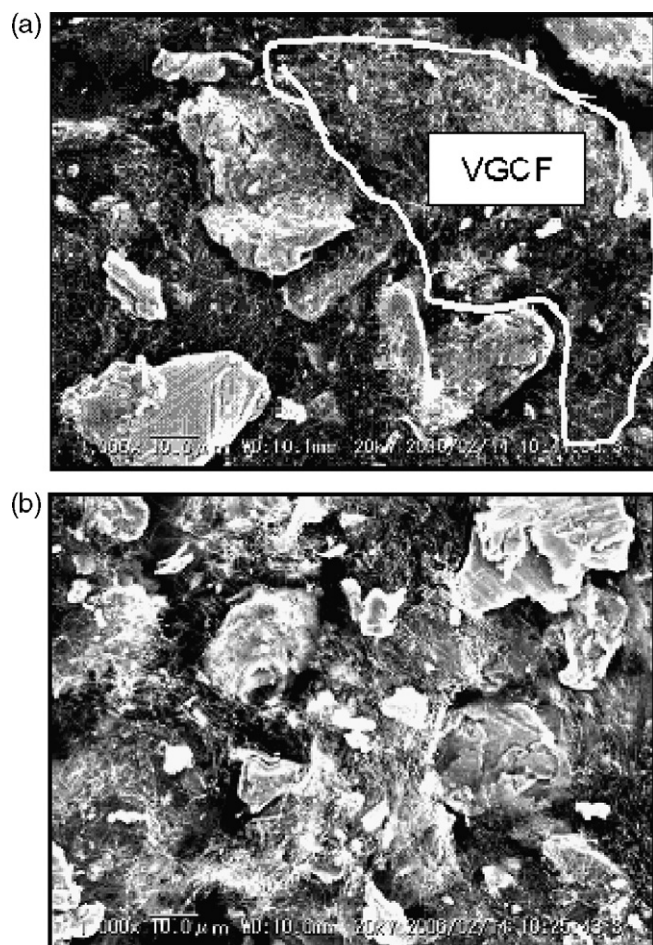| Nano-carbon | Ultrasonic | | Apparent density (g cm$^{-3}$) | Apparent conductivity (S cm$^{-1}$) |
|---|---|---|---|---|
| | Solvent | Time | | |
| VGCF | Without treatment | | 1.98 | 6.9 |
| | Ethanol | 30 min | 1.75 | 11 |
| | | 120 min | 2.29 | 7.2 |
| | Acetone | 30 min | 1.76 | 6.8 |
| | | 120 min | 2.00 | 7.1 |
| Acetylene black | Without treatment | | 1.78 | 6.3 |
| | Ethanol | 30 min | 1.92 | 9.3 |
| | | 120 min | 2.04 | 7.6 |
| | Acetone | 30 min | 2.30 | 9.4 |
| | | 120 min | 2.39 | 7.5 |

**Fig. 2.** SEM images of Fe/VGCF composite electrodes: (a) VGCF without treatment; (b) VGCF after ultrasonic treatment at 30 min in ethanol.



**Fig. 3.** The first-cycle cyclic voltammograms of Fe/VGCF composite electrodes with or without pre-treatment in ethanol. Scan rate: 1 mV s$^{-1}$, electrolyte: 3 mol dm$^{-3}$ KOH aq.

VGCF for 30 min regardless of the dispersion solvent. Such unexpected decrease of density may be due to the partial deformation of aggregate of fibrous nanostructure. A kind of fibrous portion may introduce some space inside the composite summarize.

The apparent conductivity values of the composite electrode sheets are also summarized in Table 1. These 'apparent' conductivity values contain the contribution of contact resistances, which are far smaller than the bulk resistance of electrode sheet. The conductivity values exhibit only a rough correlation with the dispersion of nano-carbons in the composite electrode, probably because the dispersion of binder (PTFE) is not controlled under the preparation condition, which significantly affects to the bulk conductance. The conductivity appears to be similar regardless of the pre-treatment conditions except for the composite with VGCF pre-treated in ethanol at 30 min, while the apparent porosity increases by the use of pre-treated nano-carbon. An electron-conductive network appears to generate by using the pre-treated nano-carbons, regardless of the condition.

Fig. 3 shows the first-cycle cyclic voltammograms of Fe/VGCF composite electrode with ultrasonic treatment of VGCF at various treatment conditions. In each voltammogram, a reduction/oxidation couple is significantly observable around −1.2 V/−0.7 V. In some cases additionally a small oxidation peak is found around −1.0 V. The current of these peaks increases over cycles, and achieves a steady-state in tens of cycles. These phenomena are observed regardless of the kind of nano-carbon, the kind of solvent, and 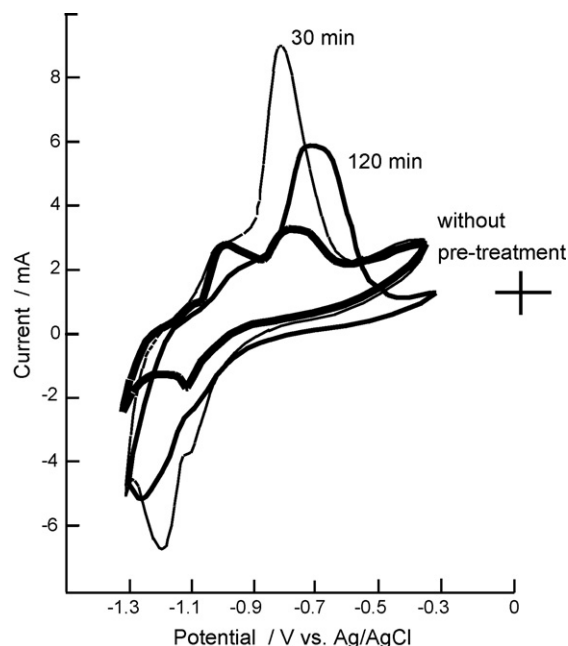the preparation condition of the composite. A reduction peak around −1.2 V is assigned to the reduction of Fe(II) to Fe(0) together with the reduction of proton to hydrogen on iron and nano-carbon surface. The assignment of the oxidation peak is perhaps complicated because several different oxidation processes have been proposed on this material. Here the authors expect that the product at the scan to −0.3 V is mainly iron hydroperoxide according to ref. [22]. The initial peak current appears to be dependent of the ultrasonic treatment time of VGCF, namely the degree of association of VGCF. The dispersion of VGCF during 30 min significantly enhances the reduction/oxidation peak current of iron. However, the ultrasonic treatment at longer time appears to provide the steep or decrease of the peak current. Such a tendency for the peak current appears to be similar to that for the apparent density of Fe/VGCF composite electrode, indicating some relationship between these two factors.

Fig. 4 shows the cyclic voltammograms of the composite electrodes of iron and VGCF (a) and acetylene black (b) dispersed in various solvents. In these cases the treatment time is 30 min. The oxidation/reduction currents on iron are influenced by the dispersion solvent for each nano-carbon material. However, the degree of the peak current enhancement by the solvent is different by the nano-carbon component. From Fig. 4(a), Fe/VGCF composite electrode with VGCF treated in ethanol shows larger peak current than the one with VGCF treated in acetone. In contrast, acetylene black treated in acetone provides larger peak current for the composite electrode than that treated in ethanol. For the composite electrode containing VGCF, the increasing order of the peak current appears to correspond to the decreasing order of the apparent density, while such a relationship is not found for the composite containing acetylene black. Among the composites shown in Fig. 4(a) and (b), Fe/VGCF with VGCF treated in ethanol exhibits the largest peak current.

From these results, it is strongly indicated that the electrochemical oxidation/reduction behavior of iron in Fe/nano-carbon composite electrode is influenced by the kind and dispersion feature of nano-carbon component even though the composite contains only 10 wt.% of nano-carbon. The nano-carbon component appears to contribute to introduce an interface among the redox
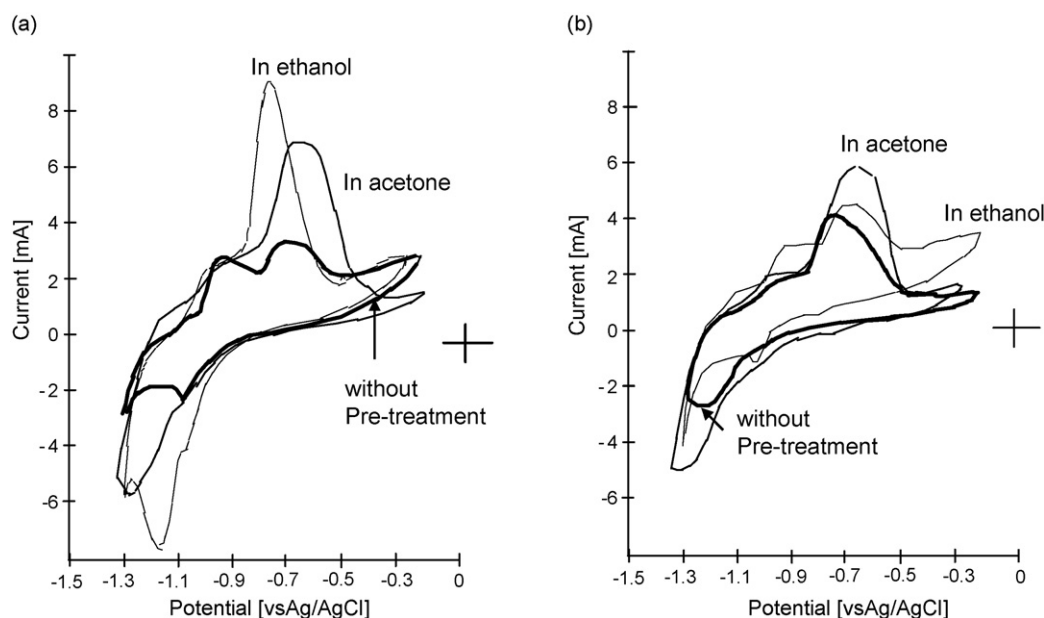
**Fig. 4.** The first-cycle cyclic voltammograms of Fe/nano-carbon composite electrodes with or without pre-treatment at 30 min: (a) Fe/VGCF; (b) Fe/acetylene black. Scan rate: 1 mV s$^{-1}$, electrolyte: 3 mol dm$^{-3}$ KOH aq.

species (Fe), electron carrier (Fe/carbon), and electrolyte, as well as to provide electron conductivity uniformly in the composite. Therefore, the space where electrode can penetrate is important to balance the three-phase interface. Within the results in the present study, the composite containing VGCF exhibits the strong dependence of internal space formation on the electrode behavior. The fibrous morphology of VGCF may be advantageous to construct an electron-conductive network and thus the exposure of the Fe/carbon connecting face to electrolyte is dominated. For the composite containing acetylene black, on the other hand, the formation of an electron-conducting network may be rather important at the content of as small as 5 wt.%.

Compared with the effect of the kind of nano-carbon and the dispersion time, the effect of the solvent used in the dispersion process is not clear in this stage. Acetone, having a lower viscosity than ethanol, is expected to disperse nano-carbons more effectively than ethanol. Therefore it is permitted to imagine that the pretreatment of VGCF in acetone may be so effective that the internal space of the composite electrode may be collapsed, while the pretreatment of acetylene black in acetone is preferable because the extent of dispersion is important for acetylene black. Otherwise, the affinity of a solvent with a rather hydrophilic/hydrophobic surface of a nano-carbon may be somewhat influenced on the structure of the composite. The precise study about such an interaction between solvent and nano-carbon surface is remained as our future work.

## 4. Conclusion

The ultrasonic dispersion of two kinds of conventional nano-carbons, acetylene black and VGCF, have been applied before they were contained in the composite electrode with iron. The electrochemical behavior of the Fe/nano-carbon composite electrode is influenced by the dispersion condition and the solvent used, and the effects of these factors are different by the kind of nano-carbon. When VGCF is applied, there appears to be optimum dispersion time, and ethanol is more favorable as a solvent than acetone. The extent of aggregation of VGCF is varied by these factors, which is considered to affect both the network of electron conduction and the interparticular space where electrolyte can immerse.

## References

[1] I. Exner, L. Kavan, S.Y. Huang, M. Grätzel, J. Power Sources 68 (1997) 720.
[2] M. Egashira, H. Takatsuji, S. Okada, J. Yamaki, J. Power Sources 107 (2002) 56.
[3] A. Chandra Bose, D. Kalpana, P. Thangadurai, S. Ramasamy, J. Power Sources 107 (2002) 138.
[4] T. Kawamura, M. Makidera, S. Okada, K. Koga, N. Miura, J. Yamaki, J. Power Sources 146 (2005) 27.
[5] K. Takada, R. Ma, M. Osada, N. Ohta, L. Zhang, T. Sasaki, J. Power Sources 146 (2005) 703.
[6] T. Doi, Y. Iriyama, T. Abe, Z. Ogumi, Chem. Mater. 17 (2005) 1580.
[7] B. Markovsky, D. Kovacheva, Y. Talyosef, M. Gorova, J. Grinblat, D. Aurbach, Electrochem. Solid-State Lett. 9 (2006) A449.
[8] S.A. Needham, G.X. Wang, H.K. Liu, J. Power Sources 159 (2006) 254.
[9] J. Morales, G. Petkova, M. Cruz, A. Caballero, Electrochem. Solid-State Lett. 7 (2004) A75.
[10] W.-K. Hu, X.-P. Gao, D. Noreus, T. Burchardt, N.K. Nakstad, J. Power Sources 160 (2006) 704.
[11] Y. Shao-Horn, S. Osmialowski, Q.C. Horn, J. Electrochem. Soc. 149 (2002) A1499.
[12] F. Bonino, in: C.A. Vincent, B. Scrosati (Eds.), Modern Batteries, John Wiley & Sons, London, 1997 (Chapter 6).
[13] D. Linden, T.B. Reddy (Eds.), Handbook of Batteries, McGraw-Hill, New York, 2002 (Chapter 25.5).
[14] B.T. Hang, M. Egashira, I. Watanabe, S. Okada, J. Yamaki, S. Yoon, I. Mochida, J. Power Sources 143 (2006) 256.
[15] B.T. Hang, T. Watanabe, M. Egashira, I. Watanabe, S. Okada, J. Yamaki, J. Power Sources 155 (2006) 461.
[16] J. Liu, A.G. Rinzler, H. Dai, J.H. Hafner, R. Kelley Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. Randall Lee, D.T. Colbert, R.E. Smalley, Science 280 (1998) 1253.
[17] G.S. Duesberg, M. Burghard, J. Muster, G. Philipp, S. Roth, Chem. Commun. (1998) 435.
[18] N. Nakashima, Y. Tomonari, H. Murakami, Chem. Lett. (2002) 638.
[19] B. McCarthy, J.N. Coleman, R. Czerw, A.B. Dalton, H.J. Byrne, D. Tekleab, P. Iyer, P.M. Ajayan, W.J. Blau, D.L. Carroll, Nanotechnology 12 (2001) 187.
[20] K. Enomoto, T. Yasuhara, K. Kato, N. Ohtake, Jpn. Soc. Mech. Eng. Int. J. 69 (2003) 309, in Japanese.
[21] E. Sato, T. Takahashi, T. Natsume, K. Koyama, TANSO 209 (2003) 159 (in Japanese).
[22] P. Periasamy, B. Ramesh Babu, S. Venkatakrishna Iyer, J. Power Sources 58 (1996) 35.