Application of FeOCl Derivatives for a Secondary Lithium Battery

III. Electrochemical Reaction and Physical State of Reaction Product of FeOCl with Aniline in Water

Kiyoshi Kanamura,* Hikari Sakaebe, Hiroyuki Fujimoto, and Zen-ichiro Takehara*

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida-honmachi, Sakyo-ku, Kyoto 606-01, Japan

ABSTRACT

The reaction product of FeOCl with aniline in water was subjected to various analyses before and after its discharge and charge to determine its physical state and electrochemical reactions. From these analyses, it can be seen that there are two possible states for the reaction product before the discharge; one is a mixture of γ-FeOOH and aniline derivatives (polymer or oligomer of aniline), and another is a mixture of γ-FeOOH and FeOOH incorporating aniline derivatives. Atomic absorption analyses during discharge and charge cycles show that the steady-state discharge and charge processes are associated with a reversible change in lithium content in the solid matrix which change corresponds to the amount of electric charge passed. The Fourier transform infrared spectra indicate that the redox reaction of aniline derivatives (doping and undoping with anions) occurs during discharge and charge cycles. These results show that aniline derivatives exist in a different state from that of a simple mixture of the states of aniline derivatives and FeOOH.

Introduction

A means for the storage of excess electric power produced at night from electric power plants or generated by solar cells is essential. For this purpose, the feasibility of large scale battery systems such as the Na-S battery and the redox flow cell has been investigated. For small power supplies for various kinds of electronic devices rechargeable lithium batteries have been developed. Rechargeable lithium batteries have the highest theoretical energy density of various conventional batteries which are operated at ambient temperature. Recently, rechargeable lithium batteries have also been considered as candidates for electric vehicles and load leveling.[1] A great amount of material is needed for such large scale applications. $LiCoO_2$ and $LiNiO_2$ have been proposed as high performance cathodes for these batteries.[2,3] However, the cost of these cathode materials is high compared with iron or manganese compounds. Iron oxides also may be a suitable material for the cathode in a rechargeable lithium battery, and various kinds of iron oxides have been investigated for such use.[4-7] However, iron oxides are usually unstable to the insertion of lithium.[4-7] The displacement of iron ions from most iron oxides has been observed during the course of the insertion of lithium. Recently, we reported that the reaction product of FeOCl with aniline in water (FAW) is a good candidate for cathode material.[8,9] FAW was prepared by the ion exchange reaction of the intercalation compound between FeOCl and aniline. FAW can be cycled many times (more than 100 cycles), and its structure and physical properties have been investigated using Fourier transform infrared spectroscopy (FTIRS), x-ray diffraction (XRD), density measurement, electron probe microanalysis, atomic absorption, and standard chemical analysis.[8,9] From these analyses, we proposed that FAW is comprised of γ-FeOOH and an aniline derivative. Compared to iron oxides, FAW has superior discharge and charge characteristics as a cathode material. Since this may be due to its physical state, the present study examined the discharge and charge of FAW to determine in more detail the physical state and the electrochemical reaction of FAW.

Experimental

The cathode material was prepared by the ion exchange reaction of FeOCl as follows. FeOCl was generated by heating a mixture of α-Fe_2O_3 and $FeCl_3$ (molar ratio: 3 to 4) at 350°C for 2 days. FeOCl (5 g) was then immersed in an aqueous solution containing 0.1 mol dm^{-3} aniline (200 cm^3) for 3 days while being stirred continuously. After this period, the reaction product was washed with water and acetone and then dried in a vacuum at 100°C. The characteristics of the reaction product before and after the discharge and charge cycle were determined by chemical analysis, atomic absorption, XRD, and FTIRS.

The cathode pellet for the electrochemical measurements was prepared by pressing a mixture of the reaction product, acetylene black, and poly(tetrafluoroethylene) in a weight ratio of 50:45:5. The discharge and charge cycle tests were performed with a standard electrochemical cell. The weight of the cathode pellet used in the cell was 50 mg and the apparent electrode area was 0.785 cm^2. Lithium foil was used for both the counter- and reference electrodes and propylene carbonate with 1.0 mol dm^{-3} $LiBF_4$ or $LiClO_4$ as the electrolyte. The discharge and charge cycle was performed under galvanostatic conditions at 0.26 or 0.064 mA cm^{-2}. All experiments were performed under a dry argon atmosphere at ambient temperature.

Results and Discussion

The FTIR spectrum of FAW has been reported in our previous paper[9] and is shown in Fig. 1, which also shows the FTIR spectra of γ-FeOOH and polyaniline. The more detailed peak assignment for the FTIR spectrum of FAW was obtained from a comparison of the FTIR spectra of FAW with those of γ-FeOOH and polyaniline in this study. The point group of γ-FeOOH is D_{2h} and its symmetry of crystal structure produces several vibration modes. The point group indicates that three lattice modes (translational modes B_{1u}, B_{2u}, and B_{3u}) can be expected to appear in the FTIR spectrum in the wave number range from 200 to 400 cm^{-1} and that three other peaks as their overtone modes should be observable in the wave number range from 400 to 800 cm^{-1}.[12] The three absorption peaks observed at 520, 600, and 720 cm^{-1} in the FTIR spectrum of γ-FeOOH were assigned to overtones of lattice modes in accordance with a standard reference.[12] The broad absorption peak was observed at 500 cm^{-1} in the FTIR spectrum of FAW, which was different from that of γ-FeOOH. This suggests that the atomic arrangements of Fe^{3+} ions and O^{2-} ions in FAW are not the same as in γ-FeOOH. This may be due to the difference in their crystal structure which in turn may be caused by the presence of hydrogen bonds in the γ-FeOOH structure. FeOCl, which does not have any hydrogen bonds in its crystal structure, has only a single broad absorption peak at ~500 cm^{-1}.[4] The absorption peak for hydrogen bonds between FeOOH layers appears at 1020 cm^{-1}.[10-13] A strong, sharp peak in the FTIR spectrum

---

* Electrochemical Society Active Member.

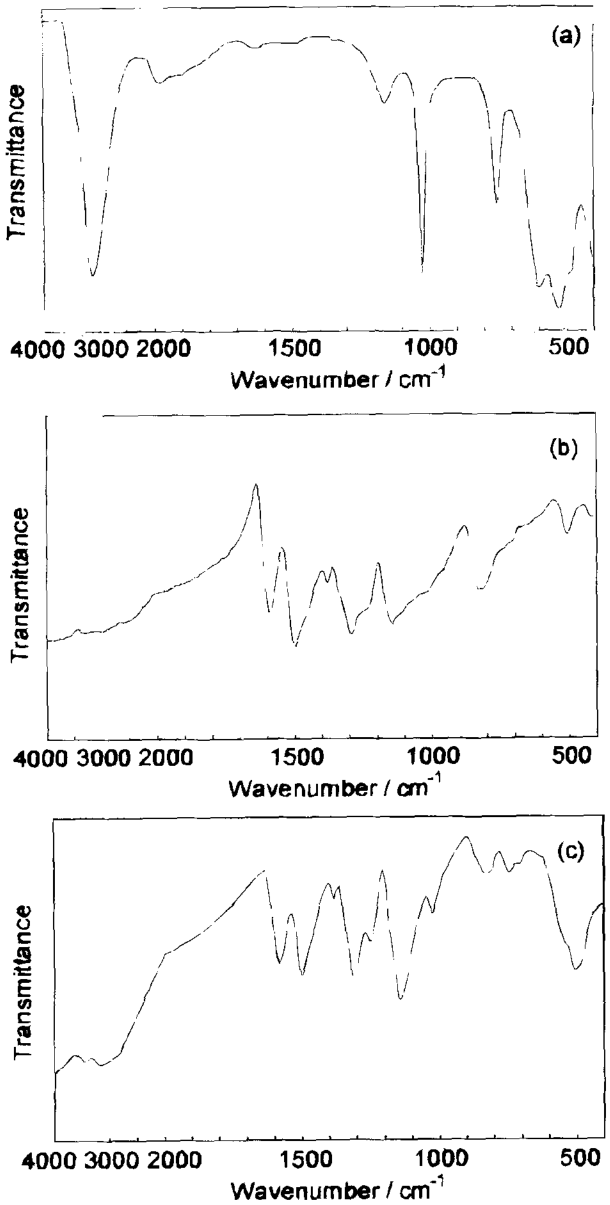

Fig. 1. FTIR spectra of (a) γ-FeOOH, (b) polyaniline (reduced form), and (c) FAW.

of γ-FeOOH was observed at 1020 cm^{-1}, indicating the presence of hydrogen bonds.[10-13] A corresponding peak was not observed in the FTIR spectrum of FAW as a strong peak, so that FAW probably does not include a substantial γ-FeOOH structure. The absorption peaks corresponding to overtones of lattice mode (Fe-O) and hydrogen bonds suggest that the FAW structure is different from the γ-FeOOH structure.

Peaks at 825, 1140, 1300, 1500, 1600, 3200, and 3400 cm^{-1} were observed in the FTIR spectrum of FAW. The peak assignments are summarized in Table I. Peaks at 825 and 3200 cm^{-1} were assigned to bending vibrations of C—H and stretching vibrations of O—H, respectively. Peaks at 1500, 1600, and 3400 cm^{-1} were assigned to bending vibrations of C—C, stretching vibrations of C═C, and stretching vibrations of N—H for secondary amine, respectively. These absorption peaks shows that secondary phenyl amines exist in FAW. Moreover, all peaks were very broad compared with aniline monomer.[9] This suggests that oligomers or polymers of phenyl amines exist in FAW as aniline derivatives.

Table I. Peak assignment for the FTIR spectrum of FAW.

Wave number (cm^{-1})	Assignment of vibration mode
3400	N—H stretching vibration
3200	O—H stretching vibration
1600, 1500	C—C ring stretching
1300	C—N stretching amine (aromatic amine)
1140	C—H in-plane bending vibration
1020	O—H—O (in γ-FeOOH) bending vibration
825	C—H out-of-plane bending vibration
740, 520, 480	Overtones of lattice modes of Fe—O

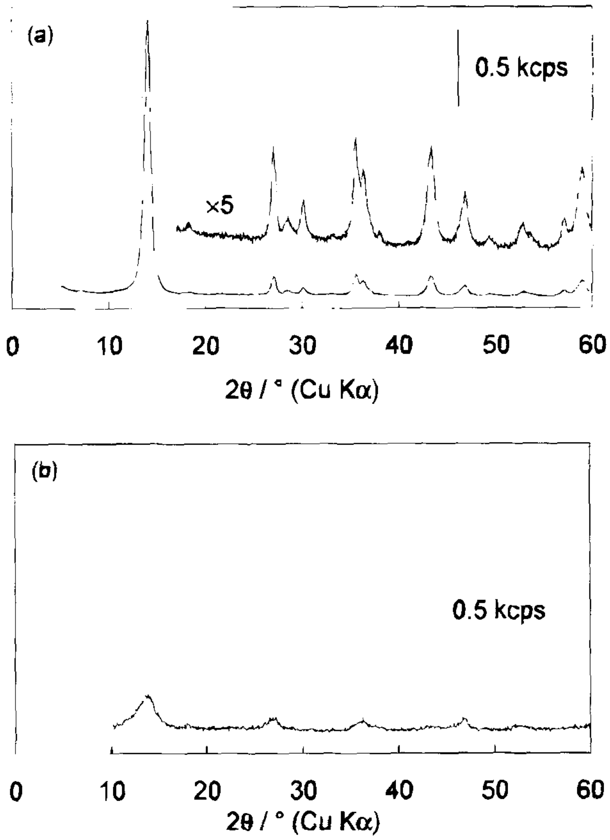

Fig. 2. XRD patterns of (a) γ-FeOOH and (b) FAW.

The crystal structure of FAW has also been investigated in our previous paper.[9] Figure 2 shows the XRD patterns of FAW and γ-FeOOH to compare results obtained from FTIR spectra with XRD analysis. The observed diffraction angles are summarized in Table II together with those for γ-FeOOH. The figures in this Table suggest that γ-FeOOH may be part of the reaction product, or that FAW has a similar structure to that of γ-FeOOH, although the peak intensities were very weak compared with high crystalline γ-FeOOH. This indicates that the amount of γ-FeOOH in FAW is a very small and/or the crystallinity of FAW is low. The half-width peak of these peaks were large. From this result, it can be seen that the crystallinity of γ-FeOOH involved in FAW is low or that FAW has a similar structure to that of less crystalline γ-FeOOH. Since the FTIR spectra also suggest that the γ-FeOOH structure is not a significant component of FAW, FAW seems to consist mainly of FeOOH with a structure similar to that of less crystalline γ-FeOOH. Other structures were not detected by XRD.

Table II. XRD peaks of γ-FeOOH and FAW.

γ-FeOOH		Reaction products	
d (Å)	[*hkl*]	2θ (degree)	*d* (Å)
6.26	020	13.85	6.39
3.29	120	26.90	3.31
2.47	031	35.80	2.51
1.937	051, 200	46.86	1.94

Table III. Chemical analysis data for FAW (weight percent).

	C	H	N	Fe	Cl	O
Product	14.34	2.05	2.79	42.70	3.24	34.88
Product[a]	15.92	2.28	3.10	47.40	—	38.72
Theoretical[b]	16.04	1.35	3.10	49.85	—	28.51

[a] After correction to FeOCl remaining in FAW, the amount of FeOCl was calculated from the amount of Cl.
[b] Calculated from the chemical formula of FeOOH + 1/4 aniline.

Table III shows the chemical analyses data for FAW where the content of Fe was determined from atomic absorption. The O content was calculated by subtraction of the sum of C, H, N, Cl, and Fe from the total content, but the detailed discussion of the Cl content in FAW was not included in our previous paper,[9] so that for this report the Cl content was taken into account for the estimation of the chemical formula of FAW. Remaining Cl may show that some FeOCl still remains after the reaction. The FeOCl content was estimated to be less than 9% of that of the Cl content. The chemical composition of FAW was recalculated by subtraction of the remaining FeOCl content from FAW. The theoretical values for FeOOH including one-quarter aniline derivatives [FeOOH(aniline derivatives)$_{1/4}$] is also shown in Table III where aniline derivatives are assumed to be polymers or oligmers of aniline. The C and Fe content of FAW was similar to that of FeOOH(aniline derivatives)$_{1/4}$, while the H and O content was larger. The amount of excess hydrogen was roughly twice as large as that of oxygen, probably due to H_2O adsorbed on the sample surface. Thus, the chemical formula of FAW is expressed by FeOOH(aniline derivatives)$_{1/4}$.

Table IV shows densities of various FeOCl derivatives and polyaniline. These values were obtained from several references.[8,9,17] The density of FAW was 2.34 g cm^{-3}, which was smaller than that of either γ-FeOOH or FeOCl. The density of the mixture of polyaniline and γ-FeOOH in a molar ratio of 1:4 was calculated and is also shown in Table IV. This value (2.97 g cm^{-3}) was larger than that of FAW. From these results, it can be seen that FAW has a more open structure than do other FeOCl derivatives. This may indicate that the main reaction product of FAW is not a simple mixture of aniline derivatives and γ-FeOOH. Such a low density further suggests that the density of the FeOOH or aniline derivatives is much smaller than that of other FeOOHs (α-FeOOH, β-FeOOH, γ-FeOOH) or polyaniline.

The main components of FAW consist of aniline derivatives and FeOOH which are different from those of α-FeOOH, β-FeOOH, and γ-FeOOH. The XRD method indicated that the intercalation compound between FeOCl and aniline was formed at the initial stage of the preparation of FAW.[9] Aniline exists in the interlayer space of FeOCl at least before the ion exchange reaction of Cl$^-$ ion with OH$^-$ ion. Therefore, there are two possibilities for the location of aniline derivatives. Aniline derivatives may escape from the interlayer space of FeOCl during the ion exchange reaction or remain in the solid matrix of FeOOH. The former case would result in a simple mixture of FeOOH and aniline derivatives, and the latter in aniline derivatives remaining in the FeOOH solid matrix. The electrochemical behavior of FAW should depend on these two possible physical states of FAW. Therefore, the electrochemical reduction and oxidation of FAW were examined. If the aniline derivatives could be shown to have a similar electrochemical behavior to polyaniline (PA) as shown in Eq. 1, the electrochemical reaction of the aniline derivatives in nonaqueous electrolyte could be explained by the doping and undoping with anions

$$\mathrm{PA}^{x+}(\mathrm{ClO}_4^-)_x + ye^- \underset{\text{charge}}{\overset{\text{discharge}}{\longleftrightarrow}} \mathrm{PA}^{(x-y)+}(\mathrm{ClO}_4^-)_{x-y} + y\mathrm{ClO}_4^- \quad [1]$$

Li$^+$ ions are not part of this redox reaction. The redox reaction of the FeOOH in FAW has never been formulated before, but it can be expected from the discharge and charge reaction of transition metal oxides to be as follows

$$\mathrm{FeOOH} + xe^- + x\mathrm{Li}^+ \underset{\text{charge}}{\overset{\text{discharge}}{\longleftrightarrow}} \mathrm{Li}_x\mathrm{FeOOH} \quad [2]$$

This redox reaction involves a change in the concentration of Li$^+$ ions in the FeOOH solid matrix. If the main reaction product of FAW is a mixture of aniline derivatives and FeOOH, these should be capable of being oxidized or reduced simultaneously, and therefore, both anions and cations being inserted or extracted into/from FAW. The measurement of the amount of Li$^+$ ions inserted or extracted into/from FAW provides information on the physical state of the reaction products as well as the reaction mechanisms of FAW.

The amounts of Li and Fe in FAW, which were discharged or charged in propylene carbonate containing 1.0 mol dm^{-3} $LiBF_4$ or $LiClO_4$, were measured by atomic absorption. The molar ratio of Li and Fe in FAW was obtained from these analyses. The amount of electrons utilized during the discharge or charge process was calculated from the electricity passed during these processes, after which the molar ratio of utilized electrons and Fe in FAW was calculated. Figure 3A shows the relationships between these two ratios during discharge and charge cycles. The discharge and charge cycle was performed under galvanostatic conditions at 0.26 mA cm^{-2}. The solid lines in Fig. 3A show the theoretical lines when the electrochemical reaction of FAW takes place according to Eq. 2. The relationship between the molar ratio of Li and Fe and that of utilized electrons and Fe in FAW for the discharge was in good agreement with the theoretical line. This indicates that lithium is inserted into the reaction product as the electric charge is passed through the cell in the course of the discharge. The relationship between these molar ratios for the charge from 0 to 80% was also in agreement with the theoretical line. However, when 100% charge was reached, the relationship deviated from the theoretical line. This suggests that a small amount of lithium remains in FAW and, that probably, some parasitic reactions take place during the last part of the first charge. The most probable side reaction is the decomposition of the electrolyte, since the potential at the end of charge was more positive than 4.2 V *vs.* Li/Li$^+$. The reversible insertion and extraction of lithium was observed in the discharge and charge cycles after the first cycle because the polarization of FAW decreased during the charge after the first discharge and charge cycle. Figure 3B also shows the relationships between the molar ratio of Li and Fe and that of utilized electrons and Fe in FAW during the discharge and charge cycle at 0.064 mA cm^{-2}. The solid lines in Fig. 3B also show the theoretical lines which were obtained assuming a one-electron reaction involving only the Li$^+$ ion. The measured values for the discharge and charge cycles were in agreement with the theoretical lines. This indicates that lithium is inserted or extracted into/from the reaction product as the electric charge is passed through the cell in the course of the discharge and charge processes. In this case, the polarization was smaller than that at 0.26 mA cm^{-2}. Thus the steady-state discharge and charge mechanisms of FAW are mostly related to the

Table IV. Densities of FeOCl, γ-FeOOH, the mixture of FeOOH and polyaniline, and FAW.

Substance	Density (g cm^{-3})	Molar volume (cm^3)
FeOCl	3.33	32.2
γ-FeOOH	4	22.2
FeOOH + 1/4 polyaniline[a]	2.97	37.7
Reaction product	2.34	53.4

[a] Assuming that a molar ratio between FeOOH and polyaniline is to be 4:1, where the density of polyaniline was estimated to be 1.5 from the reference.

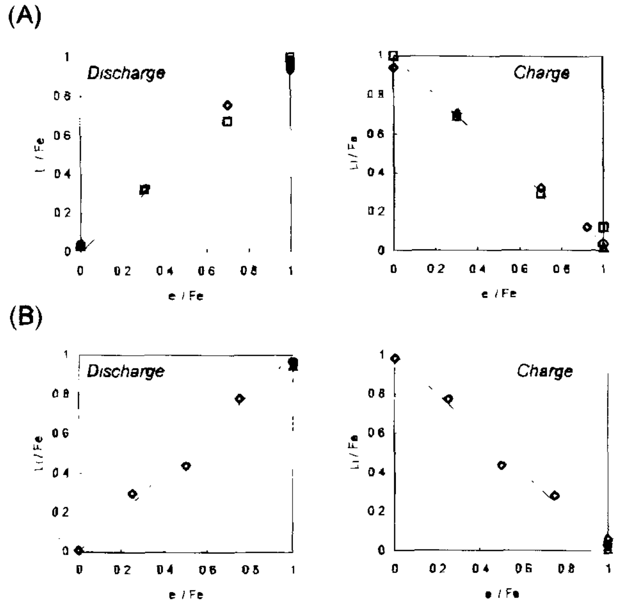

Fig. 3. Relationship between the molar ratio of Li and Fe (Li/Fe) obtained from atomic absorption for lithium and iron and the molar ratio of utilized electrons and Fe (e^-/Fe) calculated from the electric charge passed during the discharge and charge cycle. The discharge and charge current densities: (A) 0.26 mA cm^{-2} and (B) 0.064 mA cm^{-2}. The electrolyte consisted of propylene carbonate containing 1.0 mol dm^{-3} $LiClO_4$ or $LiBF_4$. ◇: during the first discharge in propylene carbonate containing 1.0 mol dm^{-3} $LiClO_4$, □: during the first discharge in propylene carbonate containing 1.0 mol dm^{-3} $LiBF_4$, ○: after the second discharge or charge in propylene carbonate containing 1.0 mol dm^{-3} $LiClO_4$, △: after the third discharge or charge in 1.0 mol dm^{-3} $LiClO_4$.

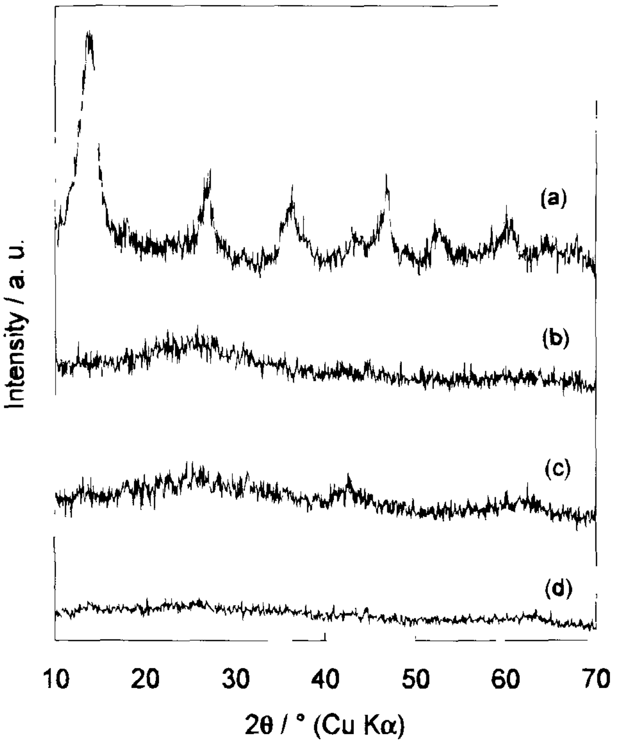

Fig. 4. XRD patterns of FAW (a) before the first discharge, (b) after the first discharge up to 50% of the theoretical capacity, (c) after the first discharge by 100% of the theoretical capacity, and (d) after the first charge, the discharge current was 0.64 mA cm^{-2}.

amount of lithium, while anions are not involved in the discharge and charge processes. Therefore, the electrochemical reaction of FAW involves the redox reaction of FeOOH. Thus, Fe^{3+} ion is reduced to Fe^{2+} ion in the course of the discharge and Fe^{2+} is oxidized to Fe^{3+}, in accordance with the lithium insertion and extraction, respectively. This result shows two possibilities. One is that polyaniline is not active in the electrochemical reaction, the other is that the main product of FAW is not a simple mixture of aniline derivatives and FeOOH.

Figure 4 shows several XRD patterns obtained in the course of the first discharge and charge cycle. The peaks observed in the XRD pattern before the discharge were similar to those of the γ-FeOOH structure. At 50% cathode depth discharge these peaks become broad and their intensities are much smaller than before the initial discharge. The XRD pattern after 100% discharge depth is similar to that after 50% discharge. Moreover, this pattern did not change after recharging and in the following discharge and charge cycles (mostly amorphous). The XRD pattern change indicates that an irreversible structural change occurs during the first discharge. This seems to be due to an increase in the amorphous nature of the FeOOH structure included in FAW. The cathode material shows excellent rechargeability (more than 100 cycles) after the first discharge and charge cycle.[14] This strongly indicates that the amorphous phase in the cathode material plays an important role in the discharge and charge characteristics. The disappearance of FeOOH was also observed from FTIR spectra. Figure 5A shows the stretching vibration mode of O—H. This peak was observed at 3200 cm^{-1} before the discharge. It then shifted to a higher wave number and overlapped with the stretching vibration mode of N-H. This change is probably due to the destruction of hydrogen bonds existing between FeOOH layers (from H—O—H to O—H), corresponding to the weak interaction between FeOOH layers. The peak corresponding to H—O—H hydrogen bonds can be observed in Fig, 5B, but its intensity was originally very weak and almost disappeared during the discharge process. This may be more evidence for the destruction of the FeOOH structure in FAW producing amorphous FeOOH. These spectra changes may be related to the change in the XRD pattern in Fig. 4.

Figure 6 shows the FTIR spectra corresponding to various vibrations for aniline derivatives during the initial discharge and charge cycle. The two peaks at 1500 and

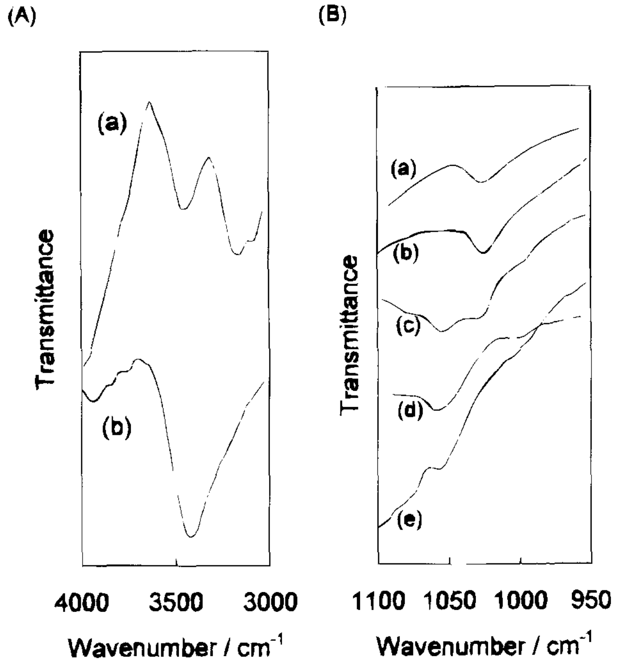

Fig. 5. FTIR spectra at around (A) 3200 cm^{-1} and (B) 1020 cm^{-1}, (a) in (A) Before the discharge, (b) at (A) after the discharge, (a) at (B) before the discharge, (b) at (B) after the first discharge (30%), (c) at (B) after the first discharge (70%), (d) at (B) after the first discharge (100%), and (e) at (B) after the first charge (100%).

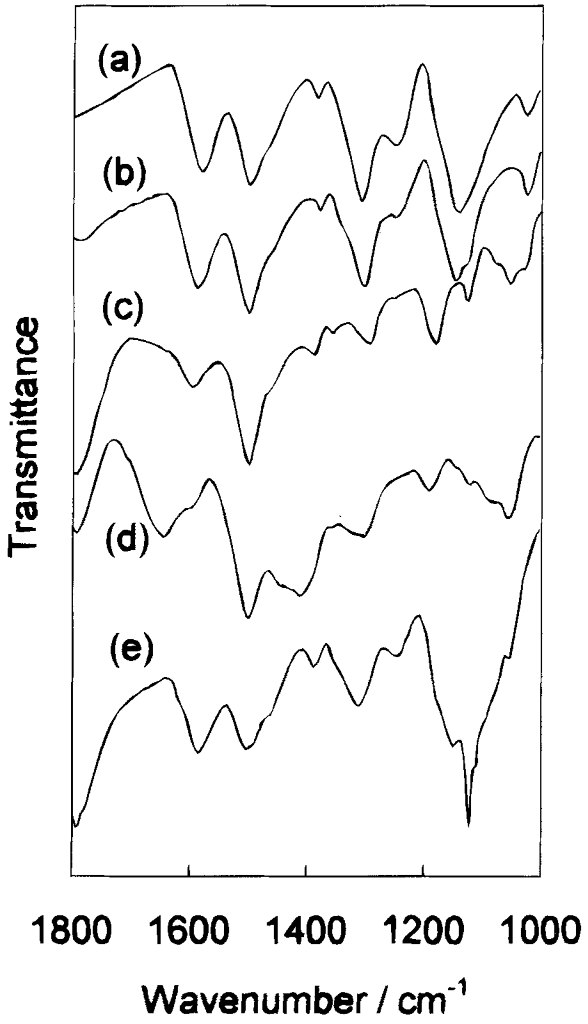

Fig. 6. FTIR spectra of the various absorptions of FAW during the discharge and charge cycle. (a) Before the first discharge, (b) after the first discharge (30%), (c) after the first discharge (70%), (d) after the first discharge (100%), and (e) after the first charge (100%).

1580 cm^{-1} correspond to the C—C stretching vibrations in an aromatic compound. Two different vibration modes were observed, while the relative intensity of these peaks changed during the discharge. After the next charge, these peaks were again clearly observed at 1500 and 1580 cm^{-1}, so that the ratio of intensity of these peaks had returned to the initial values. The C—H bending vibration in the aromatic compound was observed at 1140 cm^{-1}. This peak became broader and its intensity decreased as the discharge proceeded. After the next charge this peak returned to its original value. These spectrum changes were also observed for subsequent steady-state discharge and charge cycles, indicating that a reversible change in aniline derivatives in FAW occurs during the discharge and charge cycle. Similar changes in the absorption peaks for C—C and C—H bonds have been observed when polyaniline is discharged and charged in nonaqueous electrolyte.[15,16] Before the discharge, aniline derivatives in FAW are similar to the quinonoid form of polyaniline, and after the discharge, to the benzenoid form of polyaniline. Thus, these FTIR spectra show that the insertion or extraction of lithium into/from FAW influences the physical state of aniline derivatives during the discharge and charge cycling. This may be explained by the effect of the electronic state of FeOOH on aniline derivatives, or the strong inductive effect of the Li^+ ion inserted into FAW. If polyaniline is an active material, anions can be expected to be inserted and extracted into/from it during the cycling. However, the results obtained from atomic absorption indicate that the discharge and charge processes for FAW are totally accounted for by lithium insertion and extraction. Thus, these results cannot be explained by the assumption that the main product of FAW is a simple mixture of aniline derivatives and FeOOH.

The chemical lithiation of FAW was performed with the use of n-butyl lithium in hexane. In the course of this chemical lithiation, the formation of butane was observed. Figure 7 shows both the FTIR spectra of FAW and the reaction product of FAW with n-butyl lithium. Before chemical lithiation, there are two clear absorption peaks at 1500 and 1580 cm^{-1}, which correspond to the C—C stretching vibration in an aromatic compound. This result indicates that two C—C bonds with different chemical bond strengths exist in this aromatic compound. The absorption corresponding to the C—N stretching in this aromatic compound is observed at 1310 cm^{-1}, the strong peak at 1140 cm^{-1} represents the absorption by the C—H bending in-plane mode, and the weak peak at 825 cm^{-1} was assigned to the absorption by the C—H bending out-of-plane mode. These FTIR absorption peaks indicate that aniline derivatives are the quinonoid form which is similar to the oxidized state of polyaniline. The broad, strong peak at 500 cm^{-1} corresponds to the Fe—O bond, and the peaks at 1025 and 740 cm^{-1} represent the absorption due to γ-FeOOH. After the chemical lithiation, one peak corresponding to the C—C stretching vibration decreased, while the other increased. The absorption peak corresponding to the C—H bending in-plane mode became broader and less intense after the chemical lithiation. These changes correspond to the formation of the benzenoid form of polyaniline which is similar to a reduced state of polyaniline. This spectrum change is similar to that for polyaniline during its electrochemical reduction.[15,16] This indicates that aniline derivatives are reduced during the chemical reduction of FAW or are influenced by a strong inductive effect of the Li^+ ion. Moreover,

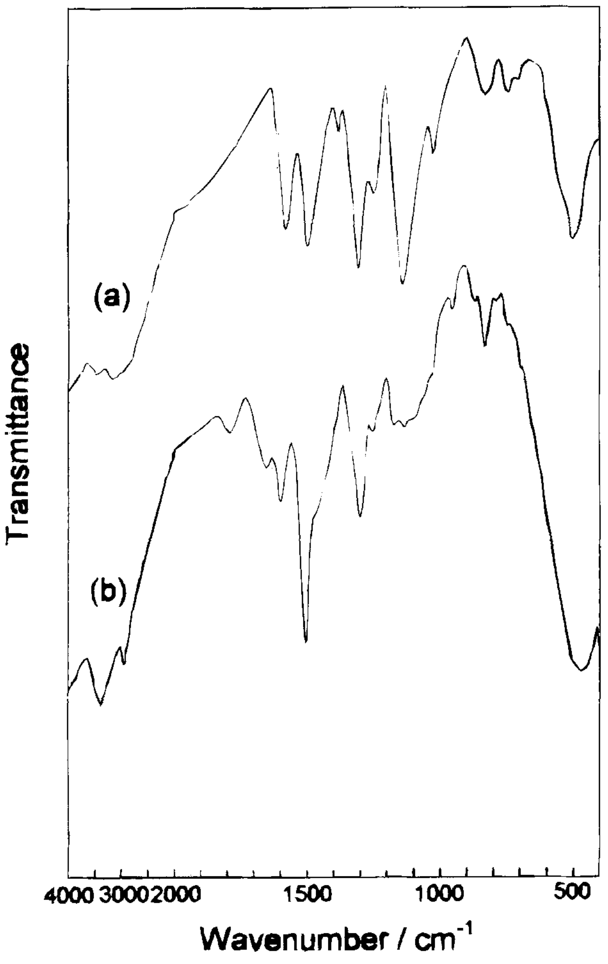

Fig. 7. FTIR spectra of (a) FAW and (b) the product of FAW with n-butyl lithium.

the FTIR spectra change for the chemical lithiation of FAW was in agreement with those for the electrochemical reduction of FAW. In chemical lithiation, only insertion of lithium should take place during the chemical reduction of FAW. The reduction of normal polyaniline would have to proceed according to Eq. 1, which is the extraction of anion from polyaniline. This means that aniline derivatives in FAW seemed to exist in a different physical state from that of normal polyaniline. It is also possible that aniline derivatives exist in the solid matrix of a-FeOOH in FAW, leading to the lithium insertion and extraction into/from FAW. Another change during chemical lithiation is the disappearance of the absorption of γ-FeOOH and the shoulder in the absorption peak of the Fe-O bond. These spectra changes can be due only to the disappearance of γ-FeOOH structure in FAW.

In summary, the redox reaction of aniline derivatives in FAW cannot be explained by the doping and undoping processes of anion. Therefore the redox reaction of aniline derivatives should be coupled with the redox reaction of the FeOOH matrix. If the main product of FAW were a simple mixture of the FeOOH and aniline derivatives, results obtained in this study could not be understood. Our results may be explained by assuming that aniline derivatives exist in the FeOOH solid matrix. Such a physical state may account for the high performance of this cathode material compared with other iron compounds.

Acknowledgment

This study has been supported by the Grant-Aid for Scientific Research from Society for Promotion of Space Science and that from the Ministry of Education, Science and Culture of Japan (No. 04750691).

Manuscript submitted Aug. 17, 1994; revised manuscript received March 7, 1995.

Kyoto University assisted in meeting the publication costs of this article.

REFERENCES

1. Z. Takehara and K. Kanamura, *Electrochim. Acta,* **38,** 1169 (1993).
2. E. Plichta, M. Salomon, S. Slane, M. Uchiyama, D. Chua, W. B. Ebner, and H. W. Lin, *J. Power Sources,* **21,** 25 (1987).
3. J. R. Dahn, U. von Sacken, and C. A. Michal, *Solid State Ionics,* **44,** 87 (1990).
4. Z. Takehara, K. Kanamura, N. Imanishi, and C. Zhen, *Bull. Chem. Soc. Jpn.,* **62,** 3609 (1989).
5. M. M. Thackeray and J. Coetzer, *Mater. Res. Bull.,* **36,** 591 (1981).
6. M. M. Thackeray, W. I. F. David, and J. B. Goodenough, *ibid.,* **17,** 785 (1982).
7. L. A. de Picciotto and M. M. Thackeray, *ibid.,* **21,** 583 (1986).
8. K. Kanamura, C. Zhen, H. Sakaebe, and Z. Takehara, *This Journal,* **138,** 331 (1991).
9. K. Kanamura, H. Sakaebe, C. Zhen, and Z. Takehara, *ibid.,* p. 2971.
10. A. Mazurkiewicz, K. Sokalski, and A. Szytula, *Phys. Status Solidi A,* **17,** K25 (1973).
11. W. B. White and R. Roy, *Am. Mineral,* **49,** 1670 (1964).
12. K. Sokalski and A. Mazurkiewicz, *Acta Phys. Pol.,* **A46,** 391 (1974).
13. T. Ishikawa, S. Nitta, and S. Kondo, *J. Chem. Soc., Faraday Trans. 1,* **82,** 2401 (1986).
14. K. Kanamura, H. Sakaebe, and Z. Takehara, *J. Power Sources,* **40,** 291 (1992).
15. T. Osaka, Y. Ohnuki, N. Oyama, G. Katagiri, and K. Kamisako, *This Journal,* **131,** 399 (1984).
16. W. -S. Huang, B. D. Humphrey, and A. J. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1,* **82,** 2385 (1986).
17. K. Kanamura, Y. Kawai, S. Yonezawa, and Z. Takehara, *J. Phys. Chem.,* **98,** 2174 (1994).