3P4-7

Synthesis of porous γ-Fe_2O_3 via alkaline treatment of size controlled scorodite particles synthesized using ultrasound irradiation and its evaluation as a cathode for lithium-ion battery

超音波照射にてサイズ制御したスコロダイト粒子から合成した多孔質 γ-Fe_2O_3 の電池特性

Yuya Kitamura[1†], Hirokazu Okawa[1], Kozo, Shinoda[2], Takahiro Kato[1], Katsuyasu Sugawara[1], and Shigeru Suzuki[2] ([1]Akita Univ.; [2]Tohoku Univ.)

北村 優弥 [1†], 大川 浩一 [1], 篠田 弘造 [2], 加藤 貴宏 [1], 菅原 勝康 [1], 鈴木 茂 [2] ([1] 秋田大院 理工; [2] 東北大 多元物質科学研究所)

1. Introduction

Iron-based materials have been studied as a cathode material for lithum-ion battery. Becase they are cheaper and more abundant than lithium cobalt oxide. Normally, maghemite (γ-Fe_2O_3) can't work as a cathode material of secondary battery because it is difficult to deintercalate lithium ion from the cathode during charge. However, nano-sized γ-Fe_2O_3 can work as a cathode material for lithium-ion battery.[1)] Recently, a simple synthesis method of nano-sized γ-Fe_2O_3 is reported that raw material, crystalline scorodite ($FeAsO_4 \cdot 2H_2O$) or strengite ($FePO_4 \cdot 2H_2O$), is just addition into an alkaline solution.[2,3)] The particles treated by alkaline solution change to a porous structure which composes of nano-sized particles of γ-Fe_2O_3. This is synthesized by the dissolution of a raw material followed by deposition of dissolved the iron ions. Therefore, we consider that the size and shape of raw material particles influence the size and shape of γ-Fe_2O_3 and the porous structure. Thus, we consider that the utilization of raw particles with spherical form relate to the synthsis of uniform size of γ-Fe_2O_3 particles because the raw material particles can be dissolved with uniform rate from the surface to core of the particles. Although crystalline scorodite is polyhedron shape, scorodite particles with spherical shape can be synthesized using stirring in sulfuric strong acidic condition under pH 0.5.[4)] However, the size of synthesized spherical particles was inhomogeneous and the size range was 10–30 μm. To synthesize uniform spherical particles, we have to control the formation timing and the amount of the crystal nuclei. In our previous study, we enabled the size control of scorodite synthesized using agglomeration effect of ultrasound irradiation in sulfuric acidic solution at pH 2.0.[5,6)] Therefore, we investigated the synthesis of uniform spherical particles using ultrasound irradiation. We also investigated the effect of size and shape of scorodite on the property of synthesized γ-Fe_2O_3. Futhermore, we evaluated porous γ-Fe_2O_3 as a cathode material for lithium-ion battery. In this manuscript, we evaluated the property and battery paformance of γ-Fe_2O_3 synthesized via alkali treatment of large scorodite particles (10 μm).

kitamura@gipc.akita-u.ac.jp (Y. Kitamura)

2. Experimental

2.1 Synthesis of scorodite using ultrasound irradiation

The Fe/As molar ratio of the Fe(II)-As(V) solution (50 mL, pH 2.0) was adjusted to 1.5. The As(V) concentration was 20 g/L. A submersible transducer (200 kHz, Kaijo) was placed on the bottom of a water-filled tank, and the flat-bottom flask containing the solution was placed directly above the transducer. Ultrasound was indirectly irradiated at 70 °C for 3 h from the bottom of flask to the solution under O_2 gas flow (100 mL/min). The precipitate was analyzed using X-ray diffraction (XRD, Ultima IV; Rigaku) measurement and scanning electron microscope (SEM, TM-1000; Hitachi) observation.

2.2 Synthesis of γ-Fe_2O_3 and its evaluation

The precipitate was obtained by the addition of the synthesized scorodite into NaOH solution. The property of precipitates was analyzed using energy dispersive X-ray fluorescence spectrometer (EDXRF, EDX-7000; Shimadzu), XRD measurement, and charge and discharge characteristic measurement system.

3. Results and Discussion

3.1 Synthesis of scorodite using ultrasound irradiation

In a scorodite synthesis process, precursor containing Fe(II) is generated by heating and oxidizing of a sulfuric acidic solution containing Fe(II) and As(V) through the oxidation using O_2 gas

flow. Scorodite is synthesized by further oxidation of the precursor [Eq. (1)].[7)]

$$4H_3AsO_4 + 4Fe(II)SO_4 + O_2 + 6H_2O \rightarrow 4Fe(III)AsO_4 \cdot 2H_2O(s) + 4H_2SO_4 \quad (1)$$

In this experiment, large scorodite particles of around 10 μm were synthesized using continuous irradiation in Fe(II)-As(V) solution (pH 2.0) for 3 h at 70 °C.[6)] Contribution of ultrasound irradiation on synthesis of the large particles is mainly following two points: i) decrease in the number of precursor particles which become crystal nuclei by the agglomeration effect of ultrasound at an early stage of experiment, ii) enhancement of oxidation of the precursor by generation of oxidants (e.g. OH radicals) [Eq. (2)] during ultrasound irradiation. Thus, large scorodite particles could be synthesized by the increase of supplied amount of solute per a nuclei.[5)]

$$Fe(II)\text{-}As(V) + OH\cdot + H^+ \rightarrow Fe(III)\text{-}As(V) + H_2O \quad (2)$$

Fig. 1 shows (a) the XRD pattern and (b) the SEM image of sample synthesized using ultrasound irradiation at 70 °C for 3 h under O_2 gas flow. The synthesized sample was identified as scorodite by XRD peaks (PDF No. 00-037-0468) [Fig. 1 (a)]. The shape and size are polyhedron and 10 μm, respectively [Fig. 1 (b)].

3.2 Synthesis of γ-Fe_2O_3 and its evaluation

Iron and arsenic are eluted from scorodite by alkali treatment, and iron deposits as γ-Fe_2O_3 just after the elution of these ions from scorodite. We confirmed the existence of Fe and As in samples before and after alkali treatment using XRF measurements (**Table 1**). The intensity of As in the sample decreased drastically after alkali treatment. This suggested that As is removed from scorodite to the solution by alkali treatment. **Fig. 2** shows that the precipitated sample after alkali treatment was maghemite (γ-Fe_2O_3). The XRD peaks of γ-Fe_2O_3 were broad because it is reported that γ-Fe_2O_3 synthesized via alkali treatment is low crystallinity due to the nano-size.[3)] Finally, we evaluated discharge capacity of the synthesized γ-Fe_2O_3, and the value was 145 mAh/g at second cycle.

In a presentation, we will show the cheracteristics of γ-Fe_2O_3 synthesized by changing the size and shape of scorodite particles. We will also show the battery performance of those synthesized γ-Fe_2O_3.

4. Conclusions

The γ-Fe_2O_3 was synthesized using alkali treatment of scorodite with large size (10 μm) which was synthesized using ultrasound irradiation. From XRF and XRD analysis, γ-Fe_2O_3 could be synthesized without impurity. The discharge capacity showed 145 mAh/g at second cycle.

Table 1 XRF intensities of Fe and As in samples before and after alkali treatment.

	NaOH treatment	
	Before	After
Fe (cps/μA)	4137	7981
As (cps/μA)	1086	12

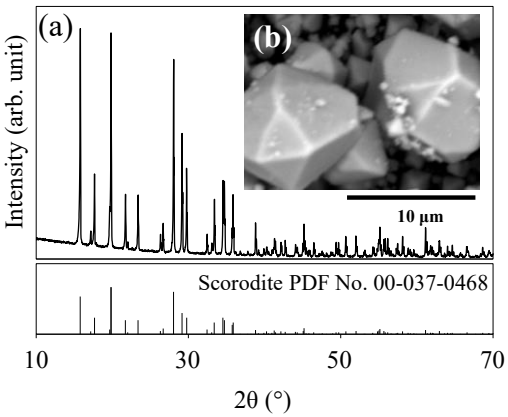

Fig. 1 (a) XRD pattern and (b) SEM image of sample synthesized using ultrasound irradiation.

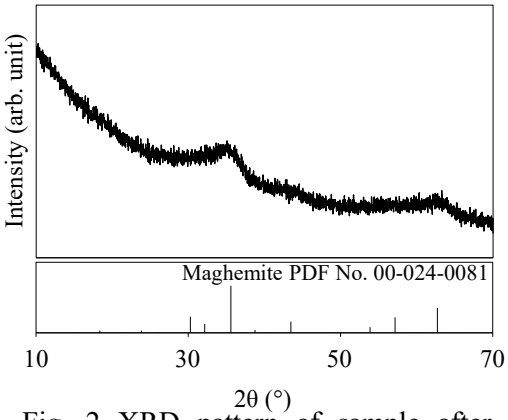

Fig. 2 XRD pattern of sample after alkali treatment of scorodite.

References

1. S. Kanzaki, et al.: J. Power Sources **146** (2005) 323.
2. T. Nakamura, et al.: Japanese patent publication 083719 (2010).
3. T. Tanno et al.: High Temp. Mater. Processes **30** (2011) 305.
4. T. Fujita et al.: Hydrometallurgy **96** (2009) 189.
5. Y. Kitamura, et al.: Jpn. J. Appl. Phys. **54** (2015) 07HE12.
6. Y. Kitamura, et al.: Ultrason. Sonochem. **35** (2017) 598.
7. K. Shinoda, et al.: Mater. Trans. **50** (2009) 1196.