Synthesis of porous γ-Fe_2O_3 from scorodite synthesized using ultrasound irradiation and evaluation of its battery performance

超音波照射を用いて合成したスコロダイトを原料とした多孔質γ-Fe_2O_3の電池特性評価

Yuya Kitamura[1†], Hirokazu Okawa[1], Kozo, Shinoda[2], Takahiro Kato[1], and Katsuyasu Sugawara[1] ([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] ([1]秋田大院 理工; [2]東北大 国際放射光イノベーション・スマート研究センター)

1. Introduction

Scorodite ($FeAsO_4 \cdot 2H_2O$) is a promising material for the storage of concentrated arsenic generated from copper smelting. Scorodite is a stable material under acidic conditions owing to its low solubility in acidic solution. The high crystallinity, lower specific surface area, and larger particle size result in lower solubility of scorodite. Large scorodite particles (>10 μm) can be synthesized at 95 °C after 7 h using a stirrer under O_2 gas flow in a sulfuric acid solution containing bivalent iron [Fe(II)] and pentavalent arsenic [As(V)].[1)] In our previous study, we synthesized the high crystallinity scorodite (10 μm) at low temperature (70 °C) for a short reaction time (3 h) by control of number of crystal nuclei using oxidation effect and agglomeration effect of 200 kHz ultrasound in sulfuric acid solution at pH 2.0.[2)] In the strongly acidic condition with pH 0.5, a low crystallinity scorodite containing amorphous was obtained when using stirring at low temperature (70 °C) and short reaction time (3 h). Whereas, highly crystalline scorodite was synthesized when using ultrasound.[3)] In addition, the shape of the scorodite particles in pH 2.0 is normally polyhedral, however, clustered-scorodite particles like a blackberry were synthesized using ultrasound at pH 0.5. The blackberry shape is not reported. Scorodite is stable in acidic solution, however, it is unstable in alkaline solution. Therefore, arsenic can be desorbed from scorodite into the solution as an arsenate ion by adding scorodite to a strong alkaline solution. Recently, it has been reported that iron and arsenic elute from scorodite in alkaline solution, and iron is deposited as porous iron oxide composed by nanosized maghemite (γ-Fe_2O_3) particles.[4)] γ-Fe_2O_3 has been studied as one of the iron-based active materials for lithium-ion battery.[5)] Iron (Fe) in iron-based active matterials is more abundant than cobalt(Co), nickelic (Ni), and manganese (Mn) used in conventional cathode active materials. We reported that porous iron oxide was synthesized using clustered-scorodite particles of approximately 4 μm diameter, which are synthesized using ultrasound irradiation. The synthesized porous iron oxide indicated an initial discharge capacity of 162 mAh/g at 0.5 C, and it showed charge-discharge cycle performance for rechargeable battery.[3)] we consider that the size and shape of raw material particles influence the size and shape of the porous structure composed by γ-Fe_2O_3. When scorodite is synthesized by a conventional stirring method at 70 °C for 3 h in pH 0.5, the crystallinity degree of synthesized scorodite was low (80%). In addition, the shape and size of the obtained particles were inhomogeneous.[3)] Ultrasound was used to control size and shape of particles.[2,3)] Therefore, we investigated the effect of particle size and shape of scorodite on the size and shape of porous iron oxide synthesized. In this study, we investigated the property, such as crystallinity, of synthesized scorodite at pH 1.0 using ultrasound. Finally, the synthesized scorodite was used as raw material for the synthesis of porous iron oxide composed by γ-Fe_2O_3 and the battery performance was evaluated.

2. Experimental

2.1 Synthesis of scorodite

The Fe/As molar ratio of the Fe(II)-As(V) solution (50 mL, pH 1.0) was adjusted to 1.5. The As(V) concentration was 20 g/L. A submersible transducer (28 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). Synthesis by stirring using a stirring blade at a stirring speed of 1000 rpm was performed to compare the result of ultrasound. These precipitate

okawa@mine.akita-u.ac.jp (H. Okawa)

samples were analyzed using X-ray diffraction (XRD, RINT2200; Rigaku) measurement and scanning electron microscope (SEM, TM-1000; Hitachi) observation.

2.2 Synthesis and battery measurement of γ-Fe_2O_3

γ-Fe_2O_3 samples were obtained using scorodite samples synthesized by the procedure 2.1. The property of synthesized samples was analyzed using energy dispersive X-ray fluorescence spectrometer (EDXRF, EDX-7000; Shimadzu), XRD measurement. Battery characteristic was evaluated using charge and discharge characteristic measurement system.

3. Results and Discussion

3.1 Synthesis of scorodite

Fig. 1 shows XRD patterns of precipitated samples treated by ultrasound and stirring. These patterns indicated that these precipitated samples were scorodite (PDF No. 00-037-0468). However, the peak intensity of the scorodite synthesized by stirring was low, and a halo pattern comes from amorphous was shown around 25–35°. The crystallinity of the scorodite was >99% (ultrasound) and 83% (stirring), respectively. In a scorodite synthesis process, precursor containing Fe(II) is initially generated by heating and oxidizing a sulfuric acid solution containing Fe(II) and As(V). Further oxidation of the precursor makes scorodite synthesized.[6)] Hence, it is considered that the halo pattern comes from amorphous iron arsenate and/or precursor containing Fe (II). Therefore, to gain the high degree of crystallinity under stirring condition, a longer reaction time >3 h is necessary. It is known that 28 kHz ultrasound has a smaller oxidation effect (i.e., lower generation amount of oxidizing radicals) than 200 kHz-frequency ultrasound; however, it has a stronger physical effect (e.g., stirring and dispersion). Therefore, it is considered that efficient oxidation of precursor enhances generation and crystallinity of scorodite by high contact surface area between O_2 bubble and the precursor particle which are miniaturized by 28 kHz ultrasound irradiation. In SEM observation, when using ultrasound, the scorodite particles were polyhedral, and most of them had a size of about 1 μm and were relatively uniform particles. On the other hand, when using stirring, bean-shaped particles of about 5 μm were observed.

3.2 Synthesis and battery measurement of γ-Fe_2O_3

In the synthesis of γ-Fe_2O_3, scorodite synthesized by ultrasound was used as a starting material. We confirmed the existence of Fe and As in samples before and after alkali treatment using XRF measurements (**Table I**). 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. XRD patterns of samples precipitated after alkali treatment was broad, however, XRD peaks of maghemite (γ-Fe_2O_3) were indicated. Finally, we evaluated the initial discharge capacity of the synthesized γ-Fe_2O_3, and the value was 170 mAh/g at 0.5C. The discharge capacity was similar to that of the previously reported γ-Fe_2O_3 which is synthesized using tufted scorodite particles (162 mAh/g). In a presentation, we will show the characteristics of porous iron oxide synthesized by changing the size and shape of scorodite particles.

4. Conclusions

γ-Fe_2O_3 was synthesized by alkaline treatment of scorodite having high crystallinity synthesized using ultrasound. From the XRD results, the synthesis of γ-Fe_2O_3 was confirmed. The initial discharge capacities by charge and discharge measurements were 170 mAh/g.

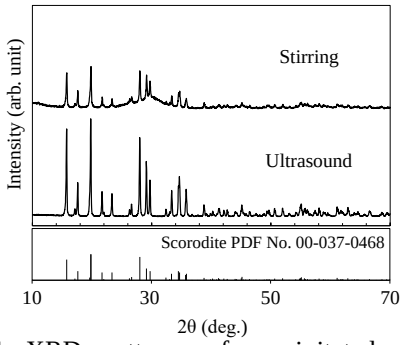

Fig. 1 XRD patterns of precipitated samples synthesized using ultrasound irradiation or stirring.

Table I XRF intensity of Fe and As in samples before and after alkali treatment.

Element	XRF intensity (cps μA^{-1})	
	Before	After
Fe	1362	2807
As	337	19

References

1. T. Fujita et al.: Hydrometallurgy **96** (2009) 189.
2. Y. Kitamura, et al.: Jpn. J. Appl. Phys. **54** (2015) 07HE12.
3. T. Tanno et al.: High Temp. Mater. Processes **30** (2011) 305.
4. S. Kanzaki, et al.: J. Power Sources **146** (2005) 323.
5. Y. Kitamura, et al.: Jpn. J. Appl. Phys. **58** (2019) SGGD03.
6. K. Shinoda, et al.: Mater. Trans. **50** (2009) 1196.