

## RESEARCH ARTICLE

# Lead acid battery with high resistance to over-discharge using graphite based materials as cathode current collector

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**Abstract**

Lead acid battery has been one of the most important battery for industry use. However, conventional lead acid battery cannot be recharged after over discharge and the performance is greatly declined. It has been revealed that the cause of not being able to be recharged is the formation of  $\alpha$ -PbO<sub>2</sub> on the surface of  $\beta$ -PbO<sub>2</sub> cathode active material due to local cell reaction between lead current collector and  $\beta$ -PbO<sub>2</sub>. Formation of  $\alpha$ -PbO<sub>2</sub> is prevented by using gold as the current collector. In this study, we developed the lead acid battery with high resistance to over discharge using graphite materials as current collector. The formation of  $\alpha$ -PbO<sub>2</sub> was prevented by using expanded natural graphite sheet as cathode current collector. The lead acid battery with current collector of expanded natural graphite sheet containing 5% polypropylene (PP) can repeat deep charge and discharge between 0 and 2 V for more than about 6 months and showed flat potential area between 1.9 and 1.3 V for every cycle. Furthermore, this battery can be charged again after over discharge for more than 4 month at the open circuit. We have succeeded to develop high performance lead acid battery.

**KEYWORDS**

graphite material, high resistance to over-discharge, lead acid battery, local cell reaction

## 1 | INTRODUCTION

Lead acid batteries have been widely used for more than 100 years.<sup>[1]</sup> They have been used for vehicles and backup power supplies and is expected as a promising energy storage devices of the future smart grid power system because of good safety, high recyclability and cost performance.<sup>[2]</sup> However, lead acid battery cannot be recharged after over-discharged, and its performance is greatly declined. Iwai

et al. have found that the above deterioration is caused by the formation of  $\alpha$ -PbO<sub>2</sub> on the surface of cathode active material  $\beta$ -PbO<sub>2</sub> due to the reduction by local cell reaction. They also have revealed that the formation of  $\alpha$ -PbO<sub>2</sub> can be prevented by using gold as cathode current collector. At that case, the lead acid battery can be recharged even after over-discharge.<sup>[3-5]</sup> Gold is expensive and not suitable for practical use. Graphite sheets have been used for gasket and heat radiation materials because of high thermal

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conductivity, high electric conductivity, physical and chemical stability, workability and so on. It can be easily get the large size with the width of 1.3 m and length of more than 100 m<sup>[6]</sup>. In this study, in order to overcome this disadvantages, we investigated the possibility of realizing the lead acid battery with high resistance to over discharge by using expanded natural graphite sheet (graphite sheet) as cathode current collector. We also tried to make graphite sheet sulfuric acid resistant by mixing various resin. It was indicated that graphite sheet can be very promising material for low cost and large size cathode current collector of lead acid battery with high performance.

## 2 | EXPERIMENTAL

### 2.1 | Manufacturing process of graphite based material

The starting material of flake graphite was soaked in mixed solution of sulfuric acid (98%) with 5% hydrogen peroxide (30%) to get sulfuric graphite of layers compound. The expanded graphite can be obtained by heating sulfuric graphite at 1000°C during 1 minute after preheating at 100°C during about 1 hour for drying. The graphite sheet can be obtained by rolling press machine. The graphite sheets with various thickness and density can be obtained by controlling pressure of press machine and weight of expanded graphite. The graphite sheet having thickness of 0.4 mm and density of 1.0 g cm<sup>-3</sup> was used for cathode current collector. We mixed four kinds of resin (polyethylene [PE], polypropylene [PP], ethylene propylene copolymer [EPM] or fluororesin [PVDF]) to the graphite sheet by 5 wt%, 10 wt%, and 15 wt% trying to improve sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) repellency. We manufactured the graphite-based material by dispersing resin materials into graphite sheet by preheating in air at 100°C for 10 minutes, and then heating at 160°C to 200°C for 10 minutes. Then, we immersed the material in sulfuric acid (47%) and measured the weight change. Also, we measured the electric resistance between front and back of the material and tensile strength in the longitudinal direction.

### 2.2 | Charge discharge experiment

We used two-electrode glass cell lead acid battery (gcLAB) for charge/discharge experiments. The cathode paste was prepared by mixing 3N  $\beta$ -PbO<sub>2</sub> powder (A Johnson Matthey) as active material, acetylene black as conductive additive and PTFE as binder at the ratio of 80:15:5 in weight. We constructed the cathode by pressing cathode paste with weight of 3.0 mg and area of 25 mm<sup>2</sup> on

each current collector. We tested six kinds of cathode current collectors (10 mm × 50 mm), Pb plate, pure graphite sheet and graphite sheet with four kinds of resin. Pure lead plate (99.9%, 10 mm × 50 mm) with effective area of 10 mm × 10 mm and sulfuric acid (35%) were used for the anode and electrolyte, respectively. Table 1 shows standard charge/discharge operation of the gcLAB. We determined charge and discharge rates by weight of cathode active material. For preparatory stabilization cycle prior to the measurement, we repeated the cycle of discharge at 9 mA g<sup>-1</sup> for 30 minutes and charge at 180 mA g<sup>-1</sup> for 20 minutes for 20 times. Next for experiment, we deeply discharged the cell down to 0 V at 9 mA g<sup>-1</sup>, opened the circuit for 48 hours or more, and we charged the cell again at 180 mA g<sup>-1</sup> for 60 minutes, then we repeated the cycle consisting of discharge at 9 mA g<sup>-1</sup> for 30 minutes and charge at 180 mA g<sup>-1</sup> for 20 minutes to study the cell performance. We carried out X-ray diffraction measurement (Rigaku Ultima-IV) in order to identify reaction material in the cathode active material after discharge. Diffracted X-ray was collected in the 2 $\theta$  range from 20° to 35° with 0.01° step for 1 second dwell time in each step and subjected to CuK $\alpha$  radiation (30 kV, 200 mA).

## 3 | RESULTS AND DISCUSSION

Figure 1A and 1B show the charge/discharge curves for the gcLAB using Pb plate and graphite sheet as cathode current collector, respectively. In the case of Pb plate, gcLAB cannot be recharged after the open circuit. On the other hand, in the case of graphite sheet, it can be recharged even after the open circuit. Figure 2A and 2B show the XRD patterns of the cathode active materials on Pb plate and graphite sheet for the current collector after the open circuit, respectively. In the case of Pb plate, XRD peak of  $\alpha$ -PbO<sub>2</sub> is observed at 2 $\theta$  = 29° similar to the previous study.<sup>[3,4]</sup> However, in the case of graphite sheet, no XRD peak of  $\alpha$ -PbO<sub>2</sub> was observed. Electrode potential does not come out for carbon in aqueous solution, so it is thought that carbon has a role of stopping the local cell reaction. From this reason, it can be explained that the formation of  $\alpha$ -PbO<sub>2</sub> is prevented on cathode active material  $\beta$ -PbO<sub>2</sub> then that the similar performance was shown when using gold as current collector. We think that graphite materials will be more advantageous than gold as current collector for lead acid batteries because of cost reduction, weight reduction and improvement of transportability. Furthermore, the use of graphite materials do not reduce recyclability.

When expanded natural graphite sheet was used as current collector, it was observed that electromotive force fluctuated high and low flutteringly as shown in Figure 1B.

TABLE 1 Standard charge/discharge operation of the gcLAB

| Number of cycle<br>Operation | 15 cycle   |            | 1 cycle   |           |          | 15cycle    |            |
|------------------------------|------------|------------|-----------|-----------|----------|------------|------------|
|                              | Discharge  | Charge     | Discharge | Rest      | Charge   | Discharge  | Charge     |
| Current                      | 9 mA/g     | 180 mA/g   | 9 mA/g    | –         | 180 mA/g | 9 mA/g     | 180 mA/g   |
| Time                         | 30 minutes | 20 minutes | 24 hours  | 48 hours. | 1 hour   | 30 minutes | 20 minutes |

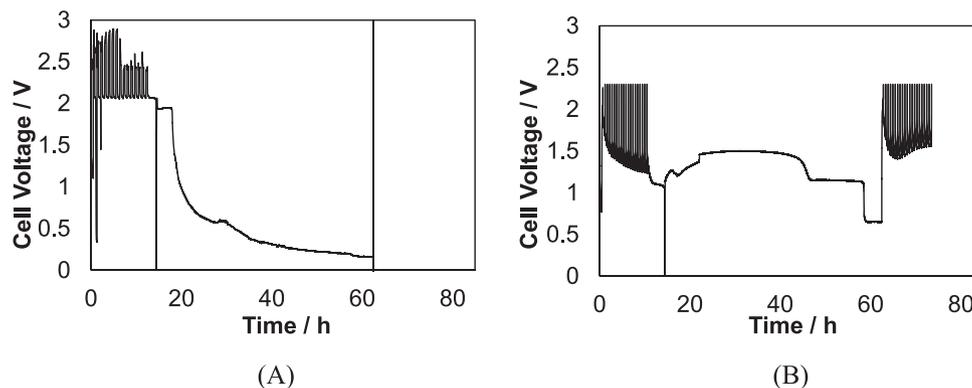


FIGURE 1 Charge/discharge curves for the gcLAB using Pb plate (A) and graphite sheet (B) as cathode current collector

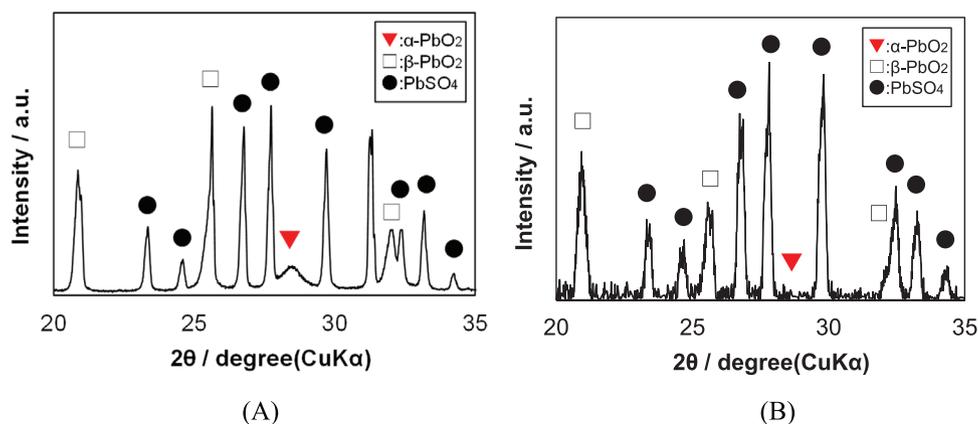


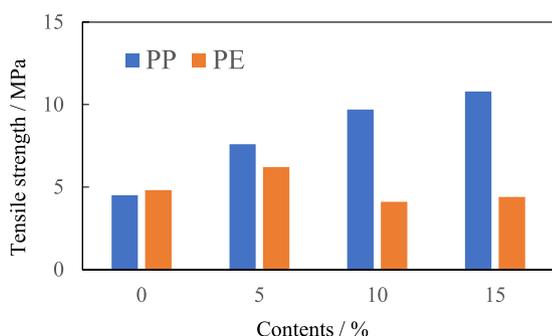
FIGURE 2 XRD patterns of cathode active materials on current collector of Pb plate (A) and graphite sheet (B) as cathode current collector

We considered this is due to swell of the graphite sheet with sulfuric acid. In order to improve sulfuric acid resistance, we tried to mix four kinds of resin (PE, PP, EPM and PVDF) to the graphite sheet. Because it was found that the resin was not dispersed uniformly into graphite even after heat treatment at 200°C in the case of EPM or PVDF, we conducted characterization for PP or PE. Figure 3 shows tensile strength for PP and PE dispersed graphite sheet by additive amount for 5%, 10% and 15%. Tensile strength of raw graphite sheet was 4.8 MPa, and graphite sheet with PP was 7.5, 9.7 and 10.8 MPa for the 5%, 10%, and 15% additive amount, respectively. It was confirmed that addition of PP gives higher tensile strength than raw graphite sheet. Tensile strength of graphite sheet with PE was 6.2, 4.1, and 4.4 MPa for the 5%, 10%, and 15% respectively. In the case

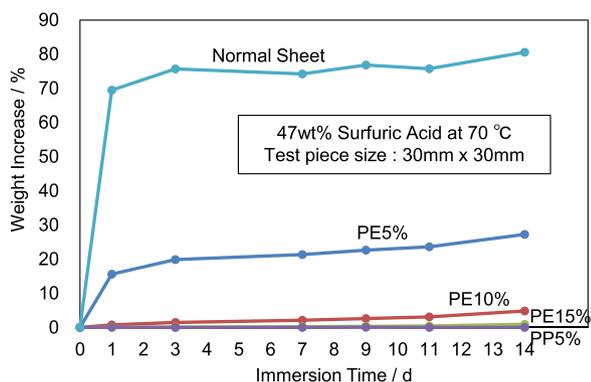
of PE, tensile strength showed the maximum value at 5% addition, but for 10% or 15% addition, it was reduced due to inhomogeneous force concentration. Table 2 shows pure water contact angle and electric resistance between front and back of PE or PP resin dispersed graphite sheet at the bulk density of 1.0 g cm<sup>-3</sup>. Contact angle of pure water was about 40° for raw graphite sheet, and over 80° for each resin dispersed graphite sheet regardless of kind of resin and addition amount. This means that dispersion of resin make water repellency increase for graphite sheet. Electric resistance between front and back of graphite sheet was about 110 mΩ for raw graphite sheet, increased with the addition amount of resin and was about 150 mΩ at 15% addition for either PP or PE. Figure 4 shows weight increase of graphite sheet with resin when immersed in

**TABLE 2** Pure water contact angle and electric resistance between front and back of PE or PP resin dispersed graphite sheet at the bulk density of  $1.0 \text{ g cm}^{-3}$

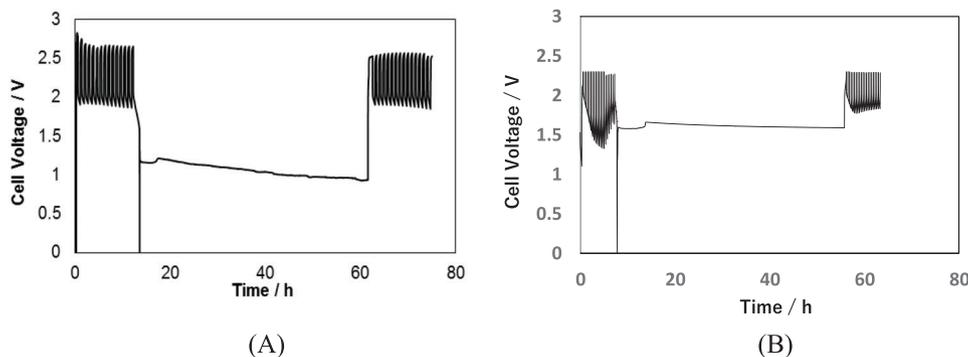
| Resin amount       | Pure water contact angle/degree |      | Resistance of front and back side of 5 mm square piece/m $\Omega$ |      |
|--------------------|---------------------------------|------|---|------|
|                    | PP                              | PE   | PP  | PE   |
| Raw graphite sheet | 39.5                            | 39.5 | <110  | <110 |
| 5%                 | 95.6                            | 98.1 | <130  | <120 |
| 10%                | 100.0                           | 84.4 | <130  | <120 |
| 15%                | 94.5                            | 89.0 | <150  | <150 |



**FIGURE 3** Tensile strength for PP and PE resin dispersed graphite sheet by additive amount for 5%, 10% and 15%



**FIGURE 4** Weight increase of graphite sheet with resin when immersed in 47% sulfuric acid at about  $70^\circ\text{C}$



**FIGURE 5** Charge/discharge experiments of the gcLAB using graphite sheet with 5% PP (A) or 5% PE (B) as current collector

47% sulfuric acid at about  $70^\circ\text{C}$ . Used test pieces were 30 mm square and width of 0.5 mm in size,  $1.0 \text{ g cm}^{-3}$  in volume density, between 0.44 and 0.50 g in weight. It is indicated that graphite sheets containing more than 5% PP and 15% PE showed no mass increase due to sulfuric acid absorption even after 14 days meaning that sulfuric acid tolerance is obtained.

Figure 5 shows the result of charge/discharge experiments of the gcLAB using graphite sheet with 5% PP (A) or 5% PE (B) as current collector. It is shown that charge/discharge cycle could restart after complete discharge to 0 V and 48 hours open circuit rest in both case. This result is very much consistent with that using raw graphite sheets. Figure 6 shows XRD patterns of the cathode active materials of the gcLAB using graphite sheet including PP (A) and PE (B) of 5%. XRD peak of  $\alpha\text{-PbO}_2$  is not observed for both case. It was found that PP and PE resin dispersed graphite sheet has a role of stopping the local cell reaction just as when using raw graphite sheet. In case of raw graphite sheet, cell voltage was fluctuating. For PP or PE case, the voltage fluctuation is well suppressed. It is thought that this is due to graphite sheet degradation by absorption of sulfuric acid and addition of PP or PE is effective to prevent the degradation. The voltage was more flat for PP case comparing with PE case. From these results, especially in improvement of tensile strength and discharge potential, it is concluded that 5% PP addition to

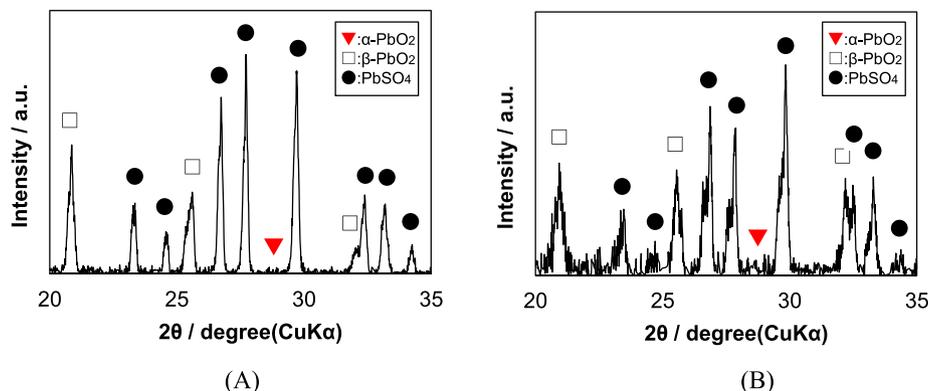


FIGURE 6 XRD patterns of the cathode active materials of the gCLAB using graphite sheet including PP (A) and PE (B) of 5%

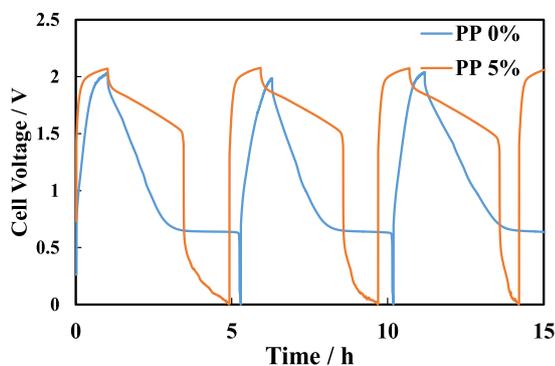


FIGURE 7 Charge/discharge curves for gCLAB using current collector of the graphite sheet including PP of 5% or 0% after the open circuit period

raw graphite sheet is most suitable for use as a cathode current collector of gCLAB.

Figure 7 shows the charge/discharge curves for gCLAB using current collector of the graphite sheet including PP of 5% or 0% when we discharged the cell at  $9 \text{ mA g}^{-1}$

to 0 V and charged at  $180 \text{ mA g}^{-1}$  for 60 minutes and repeated the cycle between 0 and 2 V after the open circuit period. Flat potential area is clearly observed between 1.9 and 1.3 V for the case of using graphite sheet including PP of 5%. Just only changing current collector from pure graphite to graphite including PP of 5%, gCLAB could repeat charge deep-discharge (between 0 and 2 V) cycle having flat potential area. It is thought to be due to sulfuric acid tolerance obtained by impregnation of PP into graphite sheet.

We tried two type of long term charge-discharge test. Figure 8A shows the result of long term charge deep discharge cycle durability test including zoomed charge/discharge curve near the beginning of the test and one near the end of gCLAB using current collector of graphite sheet including PP of 5%. One cycle is composed of 4 times repetition of full charge and discharge down to 0V, and subsequent open circuit rest for 48 hours. Charge rate was  $180 \text{ mA g}^{-1}$  and discharge rate was  $9 \text{ mA g}^{-1}$ . Either charge or discharge current was determined based on weight of cathode active material. We could continue

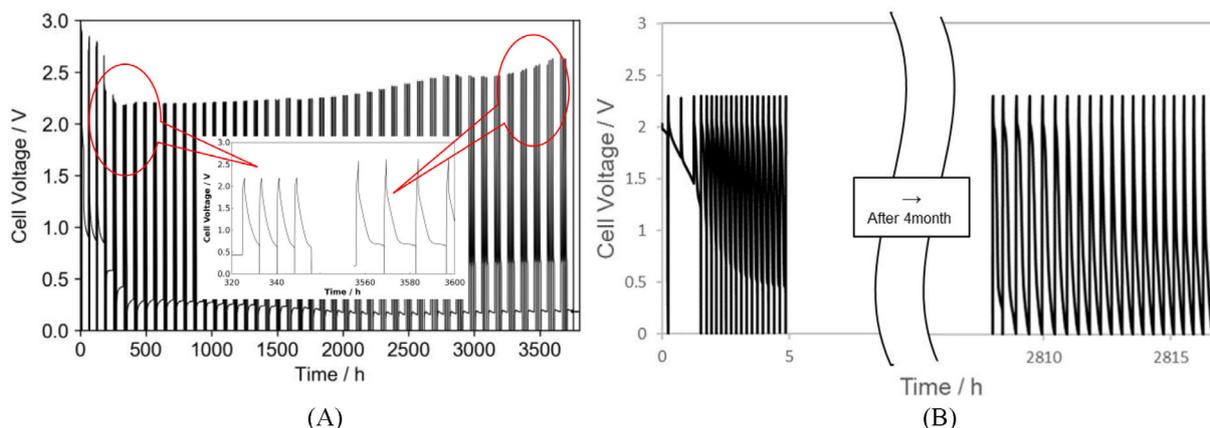


FIGURE 8 Two type of long-term charge-discharge test. A, Long term charge deep discharge cycle durability test of gCLAB, (B) the state of recharge from 4 month open circuit rest after deep discharge down to 0V for gCLAB using current collector of the graphite sheet with PP of 5%

this charge deep discharge cycle durability test for more than 5 month with no decay of charge/discharge curve, only little oxygen evolution was observed and no corrosion was observed and finally the test finished by unlucky drop of the active material. It is considered that conventional lead acid battery could not be tolerant even only one cycle. It was indicated that lead acid battery with high resistance to over-discharge is realized by using graphite based materials as cathode current collector. Figure 8B shows the state of recharge from 4 month open circuit rest after deep discharge down to 0 V for gcLAB using current collector of the graphite sheet with PP of 5%. This indicates that this type of lead acid battery can be recharged and work normally even after long term unused.

## 4 | CONCLUSION

We have developed high performance lead acid battery using graphite based composite as cathode current collector. Results were as follows.

1. Degradation of conventional lead acid battery when discharged deeply is caused by the formation of  $\alpha$ -PbO<sub>2</sub> on  $\beta$ -PbO<sub>2</sub> cathode active material due to local cell reaction between  $\beta$ -PbO<sub>2</sub> and lead current collector on cathode.
2. The formation of  $\alpha$ -PbO<sub>2</sub> was prevented by using graphite sheet as cathode current collector. This LAB can be recharged with no problem even after discharging to 0 V followed by 48 hours open circuit.
3. Characteristics of LAB was further improved by using PP dispersed graphite sheet as cathode current collector to improve sulfuric acid resistance.
4. LAB using graphite sheet containing 5% PP as current collector can repeat charge and deep discharge between 0 and 2 V cycle for more than 6 months. In the charge/discharge curve for every cycle, flat potential area between 1.9 and 1.3 V was observed.
5. LAB could be recharged from 4 month open circuit rest after deep discharge down to 0 V and worked normally.
6. We have succeeded to develop high performance LAB with high resistance to over discharge.

## DATA AVAILABILITY STATEMENT

Research data are not shared.

## REFERENCES

1. S.S. Misra, T.M. Noveske, S.L. Mraz, A.J. Williamson, *J. Power Sources*. **2001**, *95*, 162.
2. T. Huang, W. Ou, B. Feng, B. Huang, M. Liu, W. Zhao, Y. Guo, *J. Power Sources*. **2012**, *210*, 7.
3. T. Iwai, D. Kitajima, S. Takai, T. Yabutsuka, T. Yao, *J. Electrochem. Soc.* **2016**, *163*, A3087.
4. T. Iwai, M. Murakami, S. Takai, T. Yabutsuka, T. Yao, *J. Alloys Compd.* **2019**, *780*, 85.
5. T. Yao, T. Iwai, H. Tagashira, PCT patent, PCT/JP2013/74165, 2013.
6. H. Okano, M. Yoda, T. Tsujioka, T. Hosokawa, N. Misaki PCT patent, PCT/JP2015/084200, 2015.

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