

# Preparation of an electrochemically-formed spinel lithium manganese oxide and its charge–discharge behaviors

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## Abstract

Manganese hydroxides were prepared by a cathodic electrochemical precipitation from a manganese nitrate solution. The grass blade-like precipitate, which is ascribed to manganese hydroxide was 20–80  $\mu\text{m}$  long and 1–5  $\mu\text{m}$  wide and was spread out on a Pt substrate after the electrochemical precipitation. When the electrochemically precipitated manganese hydroxides were kept in an alkali metal hydroxide aqueous solution, such as NaOH, KOH and LiOH, the respective alkali metal ion was incorporated into the precipitate. Fiber-like nano-structured spinel- $\text{LiMn}_2\text{O}_4$  crystals 200 nm in diameter were obtained on a substrate by the calcination of the Li incorporated precipitate at 750 °C without any additives. The electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$  showed well-shaped CVs, even in higher scan rates. These behaviors are ascribed to the crystal size and shape of the processed spinel- $\text{LiMn}_2\text{O}_4$ .

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**Keywords:** Spinel- $\text{LiMn}_2\text{O}_4$ ; Electrochemical precipitation; Nano fiber

## 1. Introduction

Various kinds of lithium insertion compounds have been synthesized for use in rechargeable lithium batteries. Among them, spinel- $\text{LiMn}_2\text{O}_4$  has been recognized as one of the most promising cathode materials used for 4-V-class rechargeable lithium ion batteries [1–7]. The preparations of electrodes of spinel- $\text{LiMn}_2\text{O}_4$  are generally divided into two categories. In the former case, spinel- $\text{LiMn}_2\text{O}_4$  particles are mixed with some additives, such as carbon black and PVDF, and the mixture is then calendered onto a current collector. Spinel- $\text{LiMn}_2\text{O}_4$  is mostly synthesized via a calcination of manganese oxides and lithium sources, such as lithium hydroxide.[1–5,8,9] Other methods, such as sol gel and hydrothermal synthesis have been also reported with moderate success.[10,11].

In the latter category, on the other hand, spinel- $\text{LiMn}_2\text{O}_4$  is prepared directly onto electrode substrate using CVD or PVD.[6,7,12–14] In these cases, spinel- $\text{LiMn}_2\text{O}_4$  is formed

into a thin film form, which is usually used for fundamental studies on electrochemical behaviors of spinel- $\text{LiMn}_2\text{O}_4$ , but for one reason or another, has been scarcely considered for use in mass production because of its lower productivity and higher cost.

This study proposes a new preparation method for spinel- $\text{LiMn}_2\text{O}_4$  thin films using an electrochemical precipitation method of manganese hydroxide from manganese nitrate aqueous solution, followed by Li incorporation and calcination. This electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$  was examined in its electrochemical properties.

## 2. Experimental

### 2.1. Electrochemical preparation of spinel- $\text{LiMn}_2\text{O}_4$

A platinum sheet of 10 mm  $\times$  10 mm  $\times$  0.1 mm was used as a substrate. The substrate and a Pt counter electrode were set into a manganese nitrate aqueous solution to form an electrolysis cell. A constant current was applied between two electrodes for a given time at 30 °C in order to deposit

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manganese species from manganese nitrate onto the Pt substrate. A light yellowish precipitate formed on the Pt substrate after the electrochemical reduction of a manganese nitrate solution was rinsed with de-ionized water; then it was kept in an aqueous alkali metal hydroxide solution at room temperature for 1–24 h, so that the alkali ion was incorporated into the precipitate. The precipitates were then immersed in LiOH aqueous solutions of various concentrations for different times and then rinsed again with de-ionized water. They were calcined at 750 °C in the air to obtain the final product.

The characterization of the precipitates, the precursor, and the final product formed on the substrate were carried out using XRD (Rigaku RINT 2000/PC Cu Ka, 40 kV, 40 mA) and SEM (JEOL JSM-5900LV) and EDS (JED-2201) techniques. The amount of manganese in the precipitates and the products mentioned above were determined by absorbance spectroscopy, using a HITACHI Model 200-10 spectrometer.

## 2.2. Electrochemical characterization

Electrochemical behaviors of the product were examined using a three electrodes cell containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub>/PC (propylene carbonate) equipped with an Ag-wire reference electrode and an aqueous 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> solution equipped with a sat. Ag/AgCl reference electrode. Since the product adhered tightly on the Pt substrate without any particular additives, such as PVDF and acetylene black, the electrochemical measurements were carried out without further treatment.

Electrochemical measurements and galvanostatic electrolysis were carried out using a potentio/galvanostat model HSV-100 (HOKUTO DENKO) at room temperature, if the temperature is not mentioned. All reagents chemicals were used without further purification.

## 3. Results and discussions

### 3.1. Cathodic electrochemical precipitation of manganese hydroxide

To our knowledge, manganese hydroxide is usually fabricated on a substrate by chemical precipitation techniques [15], while the preparation of manganese hydroxide based on a cathodic precipitation method has not yet been reported. In our own experiments with this former method, however, greater success was found. Here, the cathodic electrochemical precipitation of nickel hydroxide on substrates from an aqueous nickel nitrate solution is a well known technique for nickel hydroxide cathode fabrication.[16,17] The electrochemical reduction of the nitrate solution increases the solution pH near to the substrate electrode surface.[16,17] This pH increase causes the cathodic precipitation of metal hydroxides on a substrate.

The processed precipitate was grown on a Pt substrate during galvanostatic cathodic reduction under conditions spec-

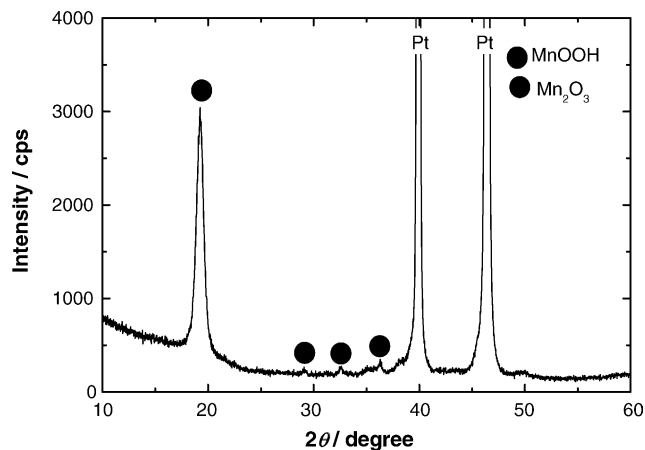


Fig. 1. XRD pattern of an air oxidized precipitate on a Pt substrate.

ified below, where the EDS analysis showed that the precipitates contained manganese. The absorption spectroscopy showed that the amount of manganese in the precipitate obtained after the galvanostatic cathodic reduction of a liquid manganese nitrate 6-hydrate for 10 min at a current density of 0.4 mA cm<sup>-2</sup> was ca. 0.1 mg. Since the melting point of Mn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O is 25 °C, the electrolysis was carried out at 30 °C.

When the precipitate was kept in the air, the color of the precipitate rapidly changed from light yellow to dark brown; also the X-ray diffraction peak of the precipitates at 2θ = ca. 19°, which implies the formation of Feitknechtite type MnOOH [18] became sharper (Fig. 1). These results indicated that the less-crystallized manganese hydroxide was initially formed on the substrate during the cathodic reduction of the manganese nitrate solution and was easily oxidized in the air.

### 3.2. Alkali ion incorporation into the electrochemically precipitated manganese hydroxides

The fresh precipitate deposited on the substrate was initially rinsed with water immediately after precipitation. Then it was immersed in various kinds of aqueous alkali metal hydroxide solutions for different durations of time. The XRD patterns of the precipitates after the immersion the aqueous solutions of 1.0 mol dm<sup>-3</sup> KOH, NaOH, and LiOH at 30 °C for 24 h revealed that Na- and K-birnessite-type manganese oxides were obtained. In contrast, Fig. 2 showed that no significant XRD peaks were observed with the precipitate immersed in an aqueous LiOH solution at 30 °C.

The precipitate immersed in a LiOH aqueous solution was rinsed with de-ionized water, and then calcined at 750 °C. Its XRD pattern shown by curve (b) in Fig. 2 is in good agreement with that of the spinel-LiMn<sub>2</sub>O<sub>4</sub>. As is shown in the next section, the cyclic voltammograms (CV) of the final product (calcined product) also indicated that the product was a spinel-LiMn<sub>2</sub>O<sub>4</sub> and that the peak current of the CV increased when increasing the immersion time of the

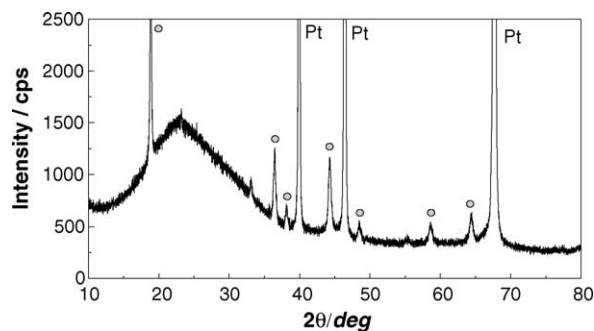


Fig. 2. XRD patterns of: (a) the LiOH treated precipitates and (b) electrochemically-formed  $\text{LiMn}_2\text{O}_4$ .

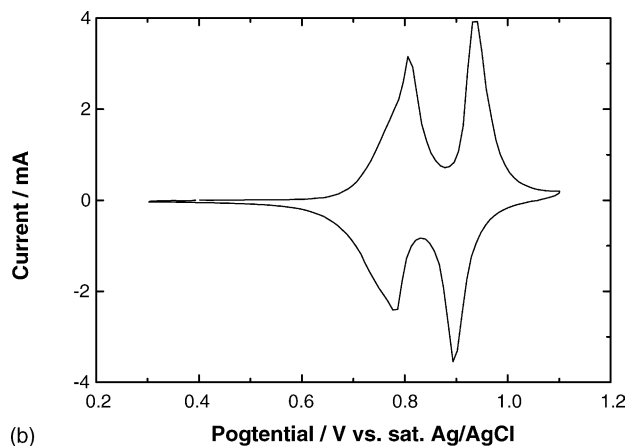
precipitate in a LiOH aqueous solution. Hereafter, we call the precipitate immersed in the LiOH aqueous solution a *spinel- $\text{LiMn}_2\text{O}_4$  precursor* and the final product an *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$* . Although the structure of spinel- $\text{LiMn}_2\text{O}_4$  precursor was not identified as a spinel structure, these results clearly shows that  $\text{Li}^+$  was incorporated into the precipitate during immersion in a LiOH aqueous solution, as well as the case of  $\text{K}^+$  and  $\text{Na}^+$  solutions.

It is clear that *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  was in direct and stable contact with the Pt substrate without any additives. The effects of the concentration of aqueous LiOH solution in which the precipitates were immersed, and where the immersion time on the yields of the *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  of the final products, were examined; the theoretical capacities of the final products on the substrate indicated that the yields of the electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$  were calculated by dividing the real capacities of the electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$ , which are estimated from the cathodic twin peaks of the CVs in the aqueous  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$  solution taken at  $10 \text{ mV s}^{-1}$ . In this calculation, the theoretical capacities of the final products on the substrate were estimated from the amount of manganese in the final product, since all the manganese was expected to exist as spinel- $\text{LiMn}_2\text{O}_4$ .

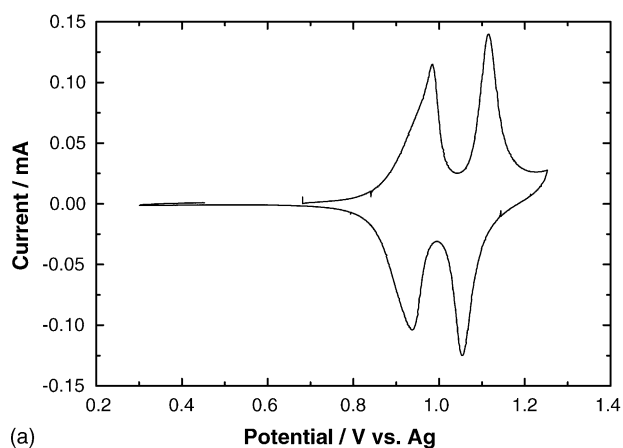
The yields are plotted against the immersion time of the precipitate in Fig. 3. Here, the yield increased with the increase of the immersion time up to ca. 12 h, whereafter the precipitates were immersed in a  $1.5 \text{ mol dm}^{-3}$  LiOH aqueous solution. When the electrochemically precipitated manganese hydroxide was immersed in a  $1.5 \text{ mol dm}^{-3}$  LiOH aqueous solution for 24 h, the yields achieved were up to ca. 80%.

### 3.3. Electrochemistry and morphology of an electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$

The curve (b) in Fig. 4 shows the CV of *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  in a  $1.0 \text{ mol dm}^{-3}$   $\text{LiClO}_4/\text{PC}$  solution at  $1 \text{ mV s}^{-1}$ , which is in good agreement with the CV obtained with typical spinel- $\text{LiMn}_2\text{O}_4$  [12,14]. The CV was also pursued in an aqueous  $1.0 \text{ mol dm}^{-3}$   $\text{LiClO}_4$  solution.



(b)



(a)

Fig. 3. Cyclic voltammograms of the electrochemically-formed  $\text{LiMn}_2\text{O}_4$  in: (a)  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$  aqueous solution at  $10 \text{ mV s}^{-1}$  and (b)  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$  PC at  $1 \text{ mV s}^{-1}$ .

As shown with curve (a) in Fig. 4, the electrode displayed well-shaped charge–discharge behaviors in this aqueous solution, even though the scan rate was 10 times higher than that in a non-aqueous electrolyte system.

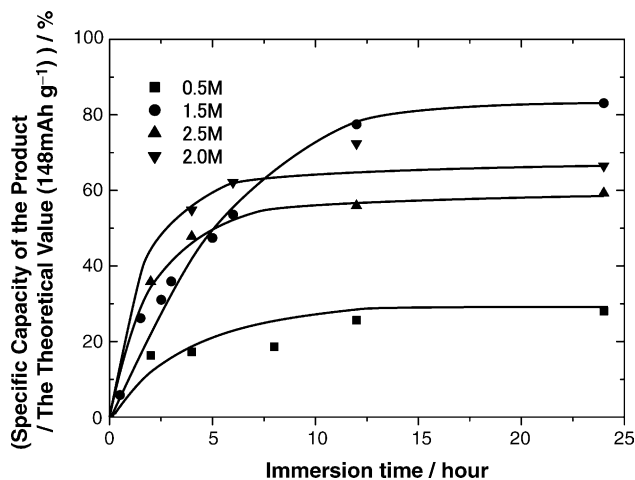


Fig. 4. Influences of immersion time on the yields of *electrochemically-formed  $\text{LiMn}_2\text{O}_4$*  at different LiOH concentration.

Martin et al. prepared tubular nanostructured-spinel- $\text{LiMn}_2\text{O}_4$  on a substrate using the template method without any additives.[19] They examined electrochemical behaviors of the tubular spinel- $\text{LiMn}_2\text{O}_4$  in an aqueous solution and reported that the smaller the diameter, the better the rate capability. Although the spinel- $\text{LiMn}_2\text{O}_4$  weight per unit area of *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  was greater than that of the tubular spinel- $\text{LiMn}_2\text{O}_4$ , the better-shaped CV was observed in the *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$* . The peak separations of the redox peaks for *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  are almost identical in diameter to those of the tubular spinel- $\text{LiMn}_2\text{O}_4$  at 230 nm. These results indicated that the spinel- $\text{LiMn}_2\text{O}_4$  electrode obtained here showed good charge–discharge performance in an aqueous system.

The CVs of *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  in PC obtained at different scan rates are shown in Fig. 5. The rate capability of the electrode almost agreed entirely with that which is reported by Mohamedi et. al.[14], where the thin film spinel- $\text{LiMn}_2\text{O}_4$  of 200 nm (prepared by electrostatic spray deposition (ESD)) was used.

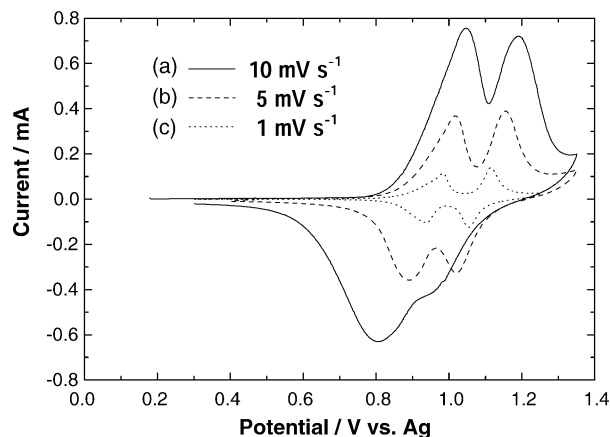


Fig. 5. Cyclic voltammograms of the electrochemically-formed  $\text{LiMn}_2\text{O}_4$  in a  $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$  taken at different scan rate. (a):  $10 \text{ mV s}^{-1}$ , (b):  $5 \text{ mV s}^{-1}$ , (c):  $1 \text{ mV s}^{-1}$ .

As shown in Fig. 6, the morphology of the precipitates and the *electrochemically-formed spinel- $\text{LiMn}_2\text{O}_4$*  were examined by SEM. The grass blade-like precipitates that were 20–80  $\mu\text{m}$  long and 1–5  $\mu\text{m}$  wide, spread out on the

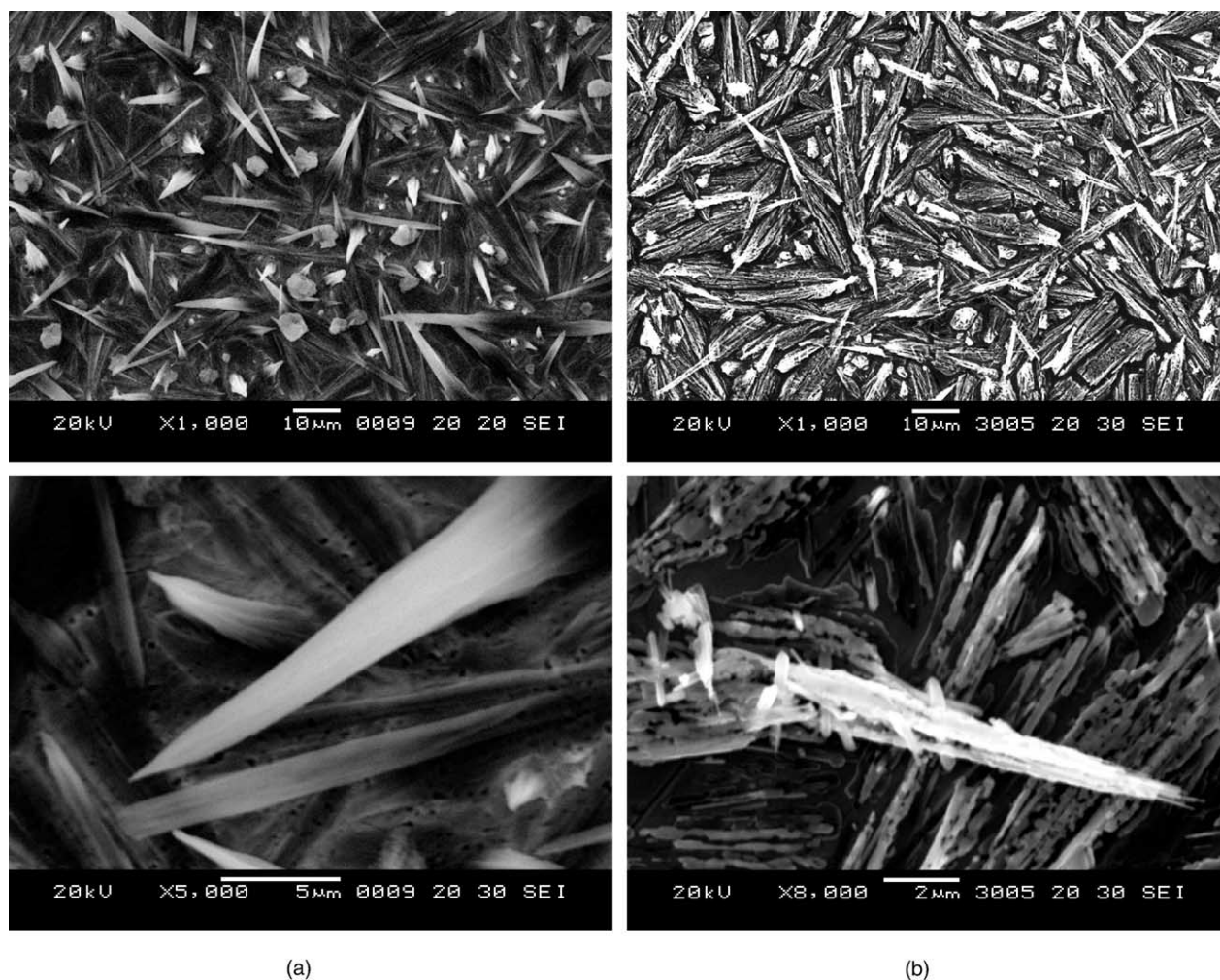


Fig. 6. SEM images of: (a) the electrochemically precipitated manganese hydroxide and (b) the *electrochemically-formed  $\text{LiMn}_2\text{O}_4$*  on a Pt substrate.



substrate after the electrochemical precipitation. Though the *electrochemically-formed spinel-LiMn<sub>2</sub>O<sub>4</sub>* inherited in the macroscopic shape and size of the precipitates, the aggregate of the nano-structured fiber-like crystals with 200 nm in width were grown during the calcination process, although its micrograph is not shown.

The preliminary experiments indicated that the electrochemical behaviors of *electrochemically-formed spinel-LiMn<sub>2</sub>O<sub>4</sub>* prepared in this study were similar to those reported for a thin film of LiMn<sub>2</sub>O<sub>4</sub>, being 200 nm thick [14]. The *electrochemically-formed spinel-LiMn<sub>2</sub>O<sub>4</sub>* is expected to be used as a positive electrode for high rate lithium ion batteries.

#### 4. Conclusion

A cathodic electrochemical precipitation method was devised to prepare amorphous manganese hydroxide on the substrate. The grass blade-like manganese hydroxide of 20–80 μm long and 1–5 μm wide was spread out on the substrate after the electrochemical precipitation. K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup> were incorporated into the electrochemically precipitated manganese hydroxide during it was immersed in the aqueous solutions involving one of each alkali metal ions, respectively.

The aggregate of the fiber-like nano-structured spinel-LiMn<sub>2</sub>O<sub>4</sub> crystals with 200 nm in diameter was obtained on a substrate by calcination of the Li-incorporated precipitate at 750 °C. The processed *electrochemically-formed spinel-LiMn<sub>2</sub>O<sub>4</sub>* was tightly attached to the substrate. The *electrochemically-formed spinel-LiMn<sub>2</sub>O<sub>4</sub>* showed well defined CVs, even in the faster scan rates.

The yields and the electrochemical properties of *electrochemically-formed spinel-LiMn<sub>2</sub>O<sub>4</sub>* were influenced by the preparation processes, such as the Li incorporation conditions. The effect of calcination temperature and electrolysis conditions will be reported in the future.

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