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# A highly-aligned lamellar structure of ice-templated $LiFePO_4$ cathode for enhanced rate capability

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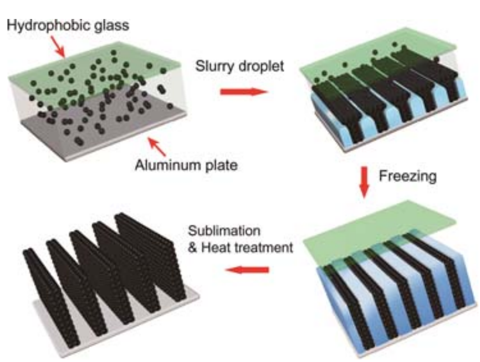
## HIGHLIGHTS

- We introduce ice-templating method to fabricate lamellar structured $LiFePO_4$ cathode.
- Lamellar structures offer larger areas for ionic conductivity and a short mean free path of electrons.
- A highly-aligned lamellar structure showed superior rate performance during the discharge.
- The lamellar structure addresses aforementioned issues and potentially applicable to the porous electrode design.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Ice-templating has been widely investigated in various energy-related fields owing to the simple and inexpensive process of this method which results highly-ordered lamellar structures. Lamellar structures offer larger active areas for ionic conductivity and a short mean free path of electrons. Here, an ice-templated $LiFePO_4$ cathode was introduced to achieve higher rate capability with a minimized carbon source. The fabricated highly-aligned porous structure demonstrates superior rate performance during the discharge process compared to electrodes which use conventional slurry casting. This enhanced performance is mainly attributed to the aligned porous structure, which facilitates the rapid transfer of electrons from the bulk to a current collector and also provides a good distribution of contact sites with Li ions in the electrolytes.



## 1. Introduction

The demand for efficient energy storage systems has led the development of advanced batteries with higher energy density levels. Li-ion batteries, as one of the most common energy storage devices, have been extensively studied as part of the effort to explore novel materials for cathodes and anodes to realize enhanced operating voltages, capacities, power, and rate capabilities, and even acceptable safety levels [1–4]. Among the parameters which determine the performance of a battery system, the rate capability is considered as most crucial, especially when devices require high-speed charge performance, such as smart mobile devices and electric vehicles [5–12]. For enhanced rate capability, the design of the electrode is crucial, as it must offer a

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**Table 1**
Carbon content of $LiFePO_4$ raw powder and carbonized LFP/PAA composite.

| Sample | Carbon content [wt%] |
|---|---|
| Raw powder (LFP-400) | 2.1 |
| After carbonization (LFP-400/carbon) | 4.4 |

**Table 2**
Specifications of the fabricated $LiFePO_4$ cathodes.

| Sample name | Preparation method | $LiFePO_4$ [wt%] | Carbon [wt%] | PVDF [wt%] | Loading [mg cm$^{-2}$] |
|---|---|---|---|---|---|
| CS_3 | Conventional slurry-cast cathode | 86.4 | 8.6 | 5.0 | 3 |
| CS_5 | | 86.4 | 8.6 | 5.0 | 5 |
| FC_3 | Ice-templated cathode | 96 | 4.0 | – | 3 |
| FC_5 | | 96 | 4.0 | – | 5 |

short mean free path of electrons and a large contact area between the active materials and the electrolytes.

The active materials used in these systems are usually coated onto a metal foil (a typical current collector) in the form of a slurry which contains conducting agents and binders along with the active materials and volatile solvents via a conventional slurry casting method [13–15]. In terms of rate performance capabilities, this conventional preparation method of electrodes using a slurry is associated with several problems, including the agglomeration and separation of the active materials during the mixing process and increased electrical resistivity mainly induced by the insulating binders used. In order to address these issues, various designs for binder-free and porous electrodes have been widely investigated to obtain high rate performance and stable cycleability [16,17].

One promising approach is to prepare highly-aligned porous structures without the use of a binder. Such an aligned structure can expand the active reaction sites to facilitate the efficient transfer of electrons through every nanostructure in the array. The void volume between the neighboring materials can also allow for easy penetration of the electrolyte, resulting in high Li-ion flux. Several studies have concentrated on developing fabrication methods for these aligned porous nanostructures [18–20]. Ice-templating, known to be an environmentally friendly and cost-effective method, is advantageous for producing aligned porous structures with various microstructural features. Morphology control of the porous structure also can be easily done by changing the solution properties and freezing conditions [21–23]. Many previous reports have shown improved performance when such devices are applied in energy devices [23–30]. Recently, the fabrication of cellular and lamellar $LiFePO_4$/C cathodes was reported [31]. However, the discussion of electrochemical properties of the lamellar structured $LiFePO_4$ is still insufficient.

Here, we suggest a well-aligned three-dimensional lamellar-structured $LiFePO_4$ electrode created via ice-templating and characterized the electrochemical performance by increasing active material loading. The ice-templated $LiFePO_4$ structure proposed here was composed of highly-aligned $LiFePO_4$ walls created by the packing of particles and macroscopic pore channels. The electrode design addresses the aforementioned issues and results in enhanced high rate capability than a conventional slurry-cast electrode. This new approach is potentially applicable to the development of porous electrode designs.

## 2. Experimental

Carbon-coated $LiFePO_4$ nanopowder (HED LFP-400, BASF) was used to create water-based slurry used here. The slurry was prepared with poly-acrylic acid (Partial sodium salt, 50 wt% solution in water, $M_w$ = 5000, Sigma-Aldrich, USA) as a dispersant system (LFP-400: PAA = 9:1 (wt.)) [32,33]. The concentration of $LiFePO_4$ powder in the final slurry was 20, 15, 10 vol%. The as-prepared slurry was dropped onto aluminum (thickness 0.25 mm, 99.999% trace metal basis, Sigma-Aldrich, USA) which was pretreated in 0.1 M phosphoric acid for 10 min as a hydrophilic treatment. Several drops on the aluminum plate (~1 cm$^2$) were covered by a hydrophobic-treated glass (Menzel-Glaser, 24 × 32 mm) and were frozen using liquid nitrogen. Subsequently, the glass was detached and the frozen sample was dried using a vacuum freeze dryer at −40 °C at 0.05 mbar for 0.5 h. When using the slurry with 15 and 20 vol% powders, the prepared slurry was stiff to fabricate the lamellar structure. For this reason, the slurry with 10 vol% powder was used to fabricate the ice-templated cathode. Finally, the freeze-dried sample was heated at a constant heating rate of 5 °C min$^{-1}$ to

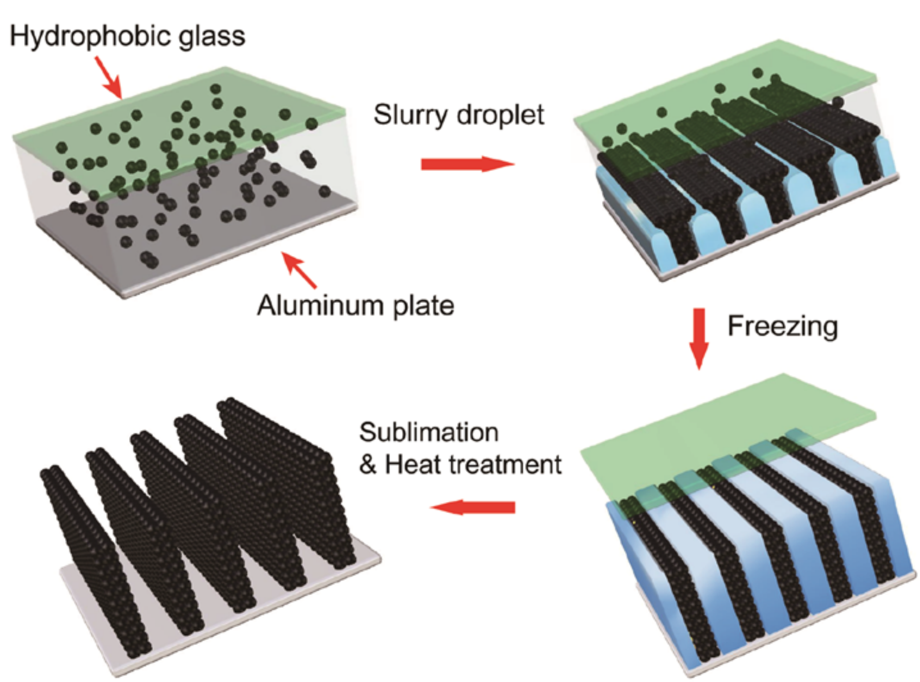


**Fig. 1.** Scheme of the fabrication process of ice-templated $LiFePO_4$ cathodes: Water-based slurry preparation, solidification, sublimation and heat treatment.