

Sustainable Reuse of FePO_4 for Charged-State Lithium Metal Battery with High Energy Density and Stable Cycle Performance

Fumiyasu Nozaki, Jinkwang Hwang,* and Kazuhiko Matsumoto*

A lithium metal-free battery (LMFB, so-called anode-free batteries) offers an ideal configuration of lithium metal batteries (LMB), theoretically achieving the highest energy density by eliminating excess lithium metal on the negative electrode. However, the limited reversibility of lithium metal deposition and dissolution prevents the stable cycling of LMFBs. In contrast, the lean LMB (LLMB) concept maintains a small amount of lithium metal on the negative electrode side, offering energy density comparable to LMFB while improving cyclability. Another advantage of LMFBs is that they do not require a lithium source in the positive electrode. Building on this, the charged-state LMB (CSLMB), which combines a charged-state positive electrode with a lean lithium metal, is introduced. Herein, the charge-state positive electrode is formed by chemically delithiating LiFePO_4 using O_2 as an oxidizing agent, while the extracted lithium is recovered as lithium acetate. This lithium can then be used to resynthesize LiFePO_4 , enabling a closed-loop lithium recycling process. Finally, the CSLMB, with its charged-state lean Li/FePO_4 full cell, demonstrates stable cycling performance and a gravimetric energy density comparable to conventional LMFBs.

1. Introduction

Lithium metal batteries (LMBs) have been one of the promising candidates to achieve high-energy-density rechargeable batteries because of the lowest redox potential (-3.04 V vs standard hydrogen electrode (SHE)) and the high theoretical capacity (3860 mAh g^{-1}) of lithium metal.^[1] The ideal LMB configuration is lithium metal-free batteries (LMFBs, so-called anode-free batteries), where all the lithium is located in the positive material and lithium metal deposits on the negative current collector during charging.^[1b,2] As a result, LMFBs can theoretically achieve

the highest energy density because they eliminate the need for excess material on the negative electrode side, thereby reducing the overall weight and volume of the cells.^[1b,3] Additionally, LMFBs can reduce manufacturing costs related to the negative electrode and alleviate safety concerns associated with excess lithium metal in typical LMBs.^[2,3] However, achieving stable cycling performance of LMFBs remains a challenge due to the loss of Li inventory during the initial charging and the limited reversibility of Li deposition/dissolution during cycling.^[1b,3b] To tackle these issues, many research groups have made modifications to current collectors and electrolytes.^[4] In addition to such modifications, lean LMBs (LLMBs) have been proposed to simultaneously enhance both the cycling performance and energy density of LMBs.^[5] The results claim that a small amount of lithium metal is employed on

the negative electrode, maintaining the energy density comparable to that of LMFBs while improving the cycling performance beyond that of LMFBs.

LiFePO_4 is gaining renewed attention due to its resource advantages, compared to layered oxide materials containing cobalt and nickel, long-term cycle stability, and high thermal stability. Recently, its application has expanded to electric vehicles.^[6] Along with the increasing use of LiFePO_4 batteries, research into recycling LiFePO_4 is also advancing.^[7] In the hydrometallurgical method, lithium is often extracted from LiFePO_4 by oxidation in an acidic solution and separated from the resulting FePO_4 . Lithium is a highly valuable element for recycling, whereas iron phosphate has limited applications for recycling. Therefore, the separated FePO_4 is often used as a raw material for reproducing LiFePO_4 .^[8] However, due to the rigid structure and outstanding cycle stability of olivine-group materials,^[9] the reuse of FePO_4 is a plausible and sustainable method.

This study proposes charged-state LMBs (CSLMBs) which are composed of a charged-state positive electrode material and a lithium metal negative electrode, achieving both the high energy density comparable to LMFBs and the relatively high cycle stability characteristic of LLMBs. Chemically delithiated FePO_4 is used as a charged-state positive electrode, and the cycling performance and energy density of CSLMBs (Li/FePO_4 configuration) are evaluated in comparison to Li-free/LiFePO_4 cell configuration. This process is intended to recover lithium from used LiFePO_4

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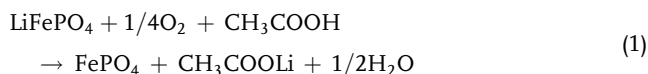
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electrodes while simultaneously reusing the resulting FePO_4 electrodes for CSLMBs.

2. Results and Discussion

A schematic illustration of the preparation route of FePO_4 is displayed in **Figure 1**. In this work, FePO_4/C is obtained from LiFePO_4/C , which is supposed to be recovered from spent batteries, through the chemical delithiation method using O_2 gas in acetic acid aqueous solution by Equation (1), as previously reported.^[10]



Here, O_2 acts as an oxidizing agent to oxidize (delithiate) LiFePO_4 , and acetic acid is added to keep the solution weakly acidic condition and to extract Li source as lithium acetate (CH_3COOLi). While the obtained FePO_4/C is used as a positive electrode for CSLMBs, the extracted lithium source during the delithiation process is supplied again for the synthesis of LiFePO_4 , enabling closed-loop lithium recycling and a more sustainable FePO_4 preparation.^[10]

Successful delithiation of LiFePO_4 using O_2 and acetic acid was verified by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) as previously reported.^[10] XRD patterns of the pristine LiFePO_4/C and obtained FePO_4/C powder shown in **Figure 2a** match that of triphylite LiFePO_4 (*Pnma*) and heterosite FePO_4 (*Pnma*), respectively.^[11] XPS spectra of the pristine LiFePO_4/C and obtained FePO_4/C in **Figure 2b** suggests that the oxidation state of FePO_4/C shifts from Fe (II) to Fe (III), confirming the oxidation of LiFePO_4 .^[12] The delithiation process was successfully achieved not only for LiFePO_4 powder but also for LiFePO_4 electrode (Figure S1, Supporting Information), demonstrating the potential applicability of this method to spent LiFePO_4 electrodes. The scanning electron microscopy (SEM) observation of the pristine LiFePO_4/C and obtained FePO_4/C powder in **Figure S2**, Supporting Information, shows similar particle morphologies, indicating the delithiation process using O_2 does not damage the morphology of the pristine particles.^[10]

Figure 3a shows the schematic comparison between LMFB using LiFePO_4 and CSLMB using FePO_4 . In the initial configuration of LMFB, LiFePO_4 in a discharged state is employed for the positive electrode without lithium metal (only a Cu current

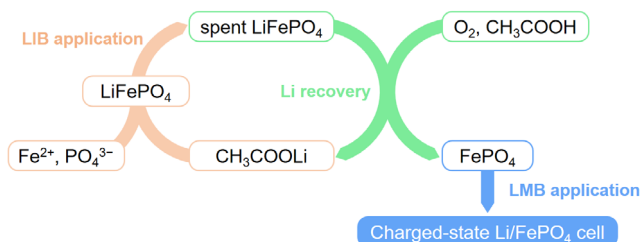


Figure 1. Schematic illustration of the production route of FePO_4 for CSLMBs and Li recovery using O_2 gas as an oxidizing agent.

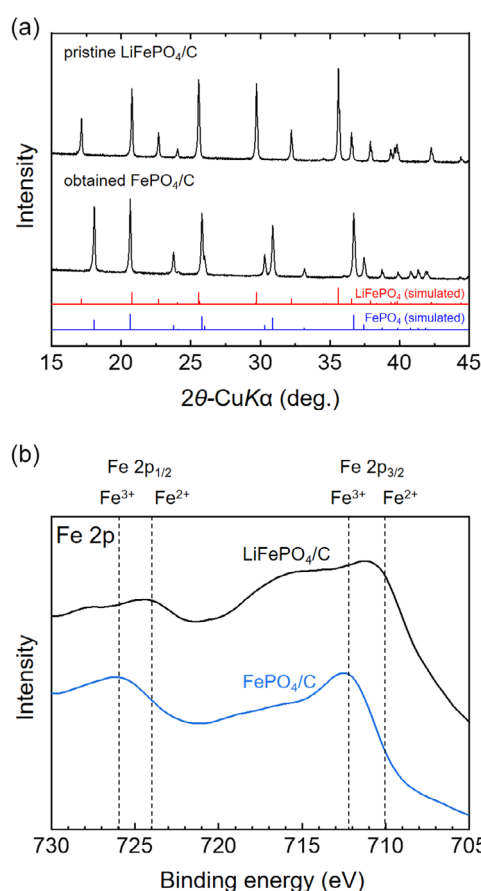


Figure 2. a) XRD patterns of the pristine LiFePO_4/C and obtained FePO_4/C . The simulated patterns are calculated based on crystallographic data in a previous report^[11] using VESTA software. b) XPS spectra of the LiFePO_4 and FePO_4 electrodes.

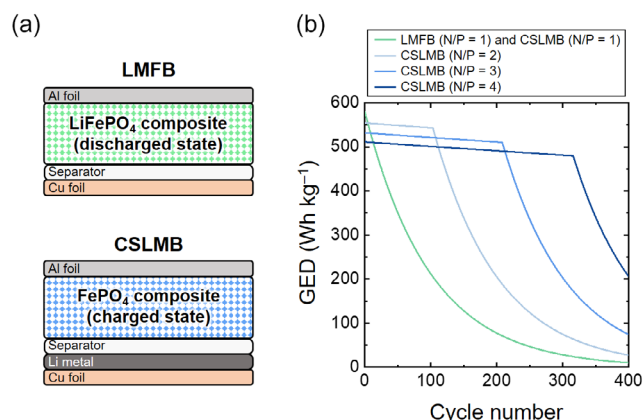


Figure 3. a) Schematic comparison between LMFB and CSLMB. b) Calculated GEDs of LMFB ($N/P = 1$) and CSLMB ($N/P = 1, 2, 3$, and 4). Detailed calculation scheme is available in Supporting Information.

collector is placed). In contrast, CSLMB consists of a charged-state FePO_4 on the positive electrode with lean lithium metal on the negative electrode.

One advantage of the CSLMBs is their excellent cycle performance, which arises from the dependency of deposited lithium states on the current collectors. In other words, the deposition of lithium metal on copper and lithium metal exhibit differences in nucleation, solid electrolyte interphase (SEI) formation, and efficiency.^[13] The Li deposition/dissolution properties on the Cu and Li electrodes will be discussed later. Another advantage of CSLMBs is the ability to load more metal, thus thicker metal, on the negative electrode compared to LMBs, because extremely thin lithium metal increases production complexities and material processing requirements. This is particularly advantageous in the cases with low N/P ratios (the ratio of negative to positive electrode capacities as explained later). For instance, assuming a positive electrode capacity of 2 mAh cm^{-2} , assembling a discharged-state LMB with N/P ratio of two would require $10 \mu\text{m}$ of lithium metal in thickness. In contrast, creating an equivalent CSLMB to the LMB would require $20 \mu\text{m}$ of lithium (Figure S3, Supporting Information), which has significantly different burdens for the commercial production of lithium metal foil. Considering that $20 \mu\text{m}$ lithium metal is recently commercially available,^[5c] CSLMBs have the potential to facilitate the fabrication of cells with lower N/P ratios more readily compared to conventional LMBs in a discharged state.

When discussing LMBs, the N/P ratio is an important factor. For instance, cells with a high N/P ratio can essentially function as half cells, leading to an exaggeration of the electrochemical performance of LMBs.^[14] Moreover, the definition of the N/P ratio for LMBs varies across studies. In a typical LMB cell configuration, the N/P ratio is often calculated using Equation (2).

$$r_{\text{N/P}} = Q_{\text{N}}/Q_{\text{P}} \quad (2)$$

Here, $r_{\text{N/P}}$, Q_{N} , and Q_{P} are the N/P ratio, the capacity of the negative electrode, and the capacity of the positive active material. The term “capacity” refers to the ability to store or release lithium. For LMFBs, the N/P ratio is defined as one in this study,^[1b] although some studies define it as zero.^[3b,4c] Similarly, the N/P ratio of CSLMBs that is equivalent to LMFBs ($\text{N/P} = 1$) is one. There is no difference in the theoretical N/P ratio between LMBs and CSLMBs, since the only difference lies in whether the lithium is initially located on the positive side or the negative side.

The gravimetric energy densities (GEDs) of LMFB and CSLMB after the n th cycle were estimated under the assumption that the Coulombic efficiency of the cell after the n th cycle ($\text{CE}_{\text{cell},n}$) is dominated by that of the positive electrode (CE_{pos}) when lithium metal remains and by that of the negative electrode (CE_{neg}) after lithium metal is depleted. Here, the CE_{pos} and CE_{neg} values are assumed to be 99.98% and 99%, respectively. As shown in Figure 3b, the GEDs of LMFB and CSLMB with $\text{N/P} = 1$ (the state of both systems is without excess lithium) significantly drop because of the irreversible lithium consumption during cycling,^[15] while the cycle life of CSLMB with $\text{N/P} \geq 2$ greatly improves because the additional lithium metal compensates for the irreversible depletion of lithium (see Supporting Information for detailed calculations).^[16] After the lithium metal is depleted, the cycling performance of CSLMB shows similar behavior to that of LMFB. As the N/P ratio increases, the total electrode weight also increases due to the additional lithium

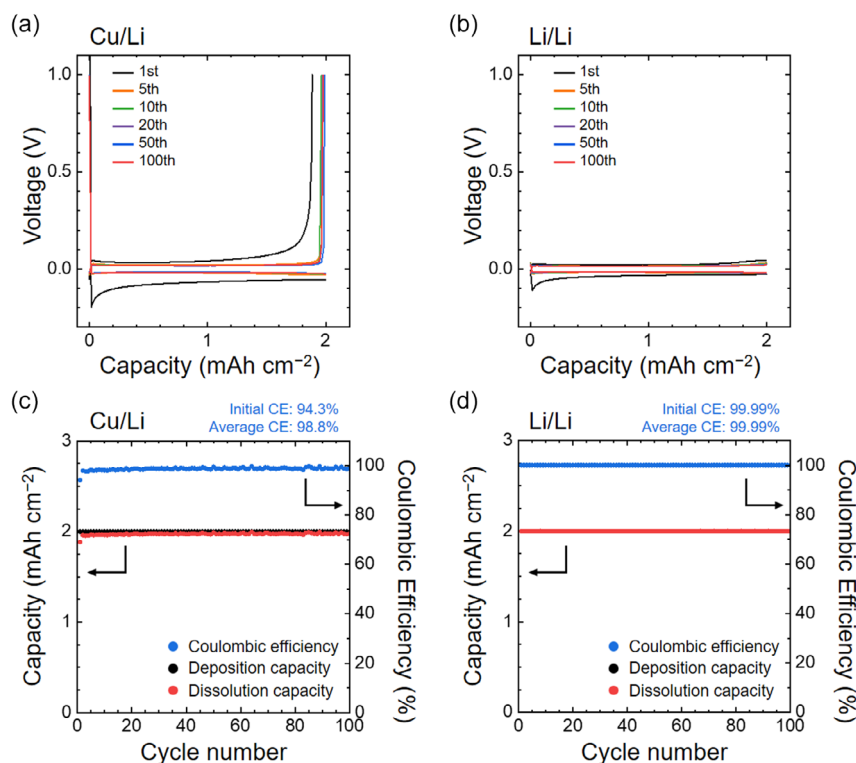


Figure 4. Galvanostatic lithium deposition/dissolution curves of a) Cu/Li and b) Li/Li cells at 1 mA cm^{-2} (2 mAh cm^{-2}). Corresponding cycle plots of c) the Cu/Li and d) Li/Li cells.

content, leading to a decrease in the maximum GED. However, the surplus lithium enhances cycling performance, indicating a trade-off between GED and cycle stability.

The aforementioned evaluation was experimentally verified. **Figure 4** shows the galvanostatic lithium deposition/dissolution curves and cycling performances of the Cu/Li and Li/Li half cells using 2 mol dm^{-3} Li[FSA]-DME (FSA: bis(fluorosulfonyl)amide and DME: 1,2-dimethoxyethane) electrolyte at 1 mA cm^{-2} . The dissolution capacity is lower than the deposition capacity in the Cu/Li cell, particularly in the first cycle (Figure 4a). The initial CE of the Cu/Li cell is 94.3% because of irreversible capacity during the initial solid SEI formation^[17] and the average CE over 100 cycles reaches 98.8%, showing a trend consistent with previous reports (Figure 4c).^[5d,15,17b] Conversely, the initial CE reaches 99.99%, and the average CE remains at 99.99% over 100 cycles in the Li/Li cell (Figure 4b,d). This stability is attributed to the additional lithium, which compensated for lithium consumption during cycles and SEI formation.^[16] Additionally, the intrinsic deposition/dissolution performance, including efficiency, nucleation process, and SEI formation, may differ between Cu/Li (metal-free cell configuration) and Li/Li (metal cell configuration); further investigation is required to draw clear factors on this point. This demonstrates the benefit of surplus lithium in maintaining high initial and cycle-averaged CEs, effectively mitigating efficiency loss due to SEI formation.

Moreover, to evaluate the electrochemical performances of CSLMBs, full cells were assembled using the FePO_4/C positive electrode, lithium metal negative electrode, and 2 mol dm^{-3} Li[FSA]-DME electrolyte. The FePO_4/C positive electrode is used here under the prospect of its reuse from spent LiFePO_4 as mentioned earlier. Additionally, lithium metal-free full cells were also fabricated using LiFePO_4/C as the positive electrode and Cu foil as the negative current collector to compare the CSLMB with a conventional LMFB. Here, three activation cycles at 0.1C ($1\text{C} = 170 \text{ mA (g-LiFePO}_4)^{-1}$ or $178 \text{ mA (g-FePO}_4)^{-1}$) were conducted before cycling tests. In the CSLMB, predischarging at 0.1C was also performed prior to activation cycles. The gravimetric values are calculated based on the total weight of positive and negative active materials. **Figure 5a** and S4, Supporting Information, show the cycle performances and charge–discharge curves of the CSLMB ($N/P = 2.50$) and LMFB at 0.3C including the initial three activation cycles at 0.1C. In the LMFB, while the initial charge capacity was close to the theoretical value, the initial discharge capacity was just 115 mAh g^{-1} . The discharge capacity continued to decrease after the second cycle, and the average CE over 100 cycles was 98.5%. This capacity decrease is related to lithium consumption due to side reactions including the SEI formation as mentioned in the lithium deposition/dissolution tests (Figure 4). In contrast, the CSLMB shows highly stable cycling performance, benefiting from the compensatory lithium metal to mitigate lithium loss during cycling.^[16] The discharge capacity of CSLMB ($N/P = 2.50$) at the 100th cycle is 140 mAh g^{-1} , while that of LMFB at the 100th cycle is 42 mAh g^{-1} . The high overpotential observed during preliminary discharge of the CSLMB shown in Figure S4b, Supporting Information, could be due to the formation of a surface layer such as $\text{LiFePO}_4(\text{OH})$ resulting from side reactions with water during delithiation process or washing.^[18] However, as cycling progresses, this layer dissipates, eliminating the overvoltage.

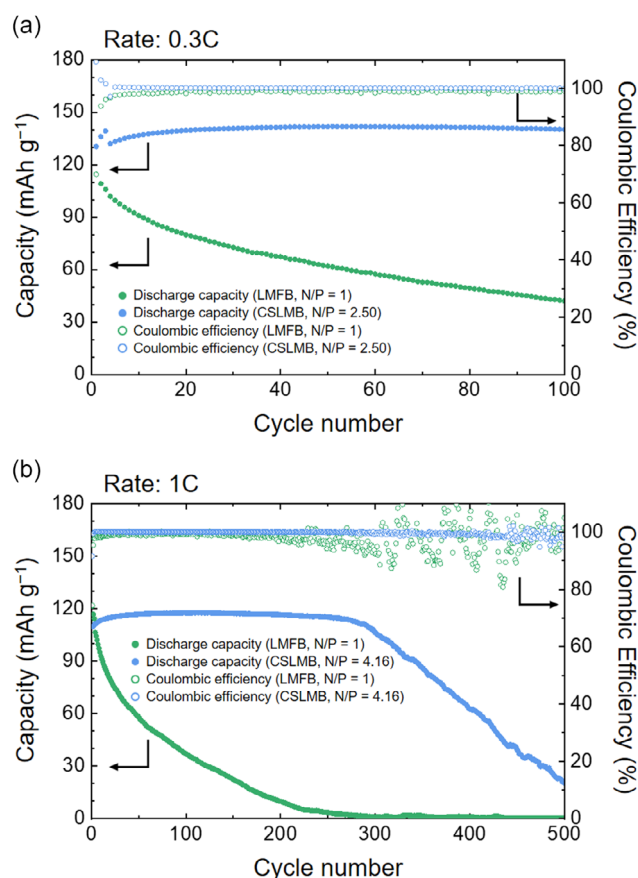


Figure 5. Cycle performances of a) LMFB and CSLMB ($N/P = 2.50$) at 0.3C including initial three activation cycles at 0.1C and b) LMFB and CSLMB ($N/P = 4.16$) at 1C including initial three activation cycles at 0.1C. Capacity is calculated based on the total weight of positive and negative active materials.

The longer cycling performance was also evaluated. Figure 5b and S5, Supporting Information, demonstrate the cycle performances and charge–discharge curves of the CSLMB ($N/P = 4.16$) and LMFB at 1C including the initial three activation cycles at 0.1C. In the LMFB cell, the capacity drops to nearly zero after 300 cycles, whereas the CSLMB cell demonstrates stable cycling performance up to around 300 cycles. Beyond 300 cycles, the CSLMB cell experiences a rapid decline similar to that observed in the LMFB cell. This sharp decrease is attributed to the depletion of lithium at the negative electrode, resulting in irreversible lithium consumption and the deterioration of capacity retention.

The GEDs corresponding to Figure 5 and the CSLMB ($N/P = 1$) are shown in Figure S6, Supporting Information. As suggested by the calculations (Figure 3b), the GEDs of LMFB and CSLMB ($N/P = 1$) significantly decrease with each cycle, while the CSLMB ($N/P \geq 2$) maintains a relatively high GED. Even after the first cycle, the GEDs of LMFB and CSLMB ($N/P = 1$) fall below 400 Wh kg^{-1} , which is smaller than that of the CSLMB ($N/P \geq 2$). The CSLMB ($N/P = 2.50$) achieves a stable GED of more than 450 Wh kg^{-1} over 100 cycles at 0.3C (Figure S6a, Supporting Information), whereas the GED of

CSLMB with a higher N/P ratio of 4.16 operated at 1C is below 400 Wh kg⁻¹ (Figure S6b, Supporting Information). The decrease is explained by the increase in N/P ratio and current density, resulting in the heavier total mass of active materials and the lower specific capacity, respectively. The GED of CSLMB (N/P = 4.16) demonstrates stable values over 300 cycles and then drops significantly. This aligns well with the result from the calculation (Figure 3b).

3. Conclusion

This study demonstrated the concept of CSLMB, where the initial cell configuration consists of a charged-state positive electrode (FePO₄) with a lean lithium metal negative electrode. Compared with LMFBs, CSLMBs showcased superior cycle stability and higher energy density owing to the additional lithium metal compensating for the irreversible loss of Li inventory during cycling. In addition, a Li source extracted during the delithiation process of LiFePO₄ can be recovered and then used to resynthesize LiFePO₄, realizing the closed-loop Li recycling. This potential approach could involve the recycling of LiFePO₄ electrodes to recover Li source while utilizing the remaining FePO₄ for CSLMB applications. Degradation in graphite/LiFePO₄ full cells is reported to primarily stem from the graphite side, with minimal degradation in the LiFePO₄ itself.^[9d,19] Thus, FePO₄ obtained from used LiFePO₄ could exhibit sufficient performance. The state of charge (SOC) of used LiFePO₄ electrodes is expected to be nonuniform, but this process allows all materials to be recovered as FePO₄ regardless of the SOC.

Although the production of thin lithium metal foil is still challenging, CSLMBs require thicker lithium metal than LMBs in the initial state under the condition of the same N/P ratio due to the complete loading of lithium on the negative electrode, providing an advantage in lithium metal film production. CSLMBs could be promising as a means of enhancing cycle stability and energy density in LMBs. However, it is important to note that there is a trade-off between cycle performance and the energy density of CSLMB. The cell design, including the amount of lithium metal, can be adjusted based on the desired balance between energy density and cycle performance. Additionally, improving the low deposition/dissolution efficiency of lithium metal, which is a common challenge in LMBs, is crucial for enhancing the cycle stability of CSLMB.

4. Experimental Section

Preparation of FePO₄: To prepare FePO₄, LiFePO₄ was chemically delithiated according to the previously reported method.^[10] Commercial carbon-coated LiFePO₄ (LiFePO₄/C, 4.00 g, 25.1 mmol) (Toshiba Manufacturing, purity 99.9%, carbon coating: 1.15%), acetic acid (CH₃COOH, 1.83 g, 30.5 mmol) (Fujifilm Wako Pure Chemicals, purity 99.7%), and distilled water (200 cm³) were added into an air-tight glass reaction vessel (volume: 1.2 dm³). The vessel was evacuated and 1.5 atm of O₂ gas was introduced. After the mixture was stirred for 72 h, the delithiated product (FePO₄/C, 3.73 g, 24.4 mmol) was obtained by centrifuging, washing with distilled water several times, and then drying overnight at 80 °C under a vacuum.

Characterizations: XRD patterns of the LiFePO₄/C and FePO₄/C were collected using a Rigaku SmartLab diffractometer (Ni filtered Cu-Kα,

40 kV, 30 mA, scan rate: 0.3° min⁻¹). XPS of the LiFePO₄ and FePO₄ electrodes were analyzed using a JEOL photoelectron spectrometer (JPS-9030, Mg-Kα). Before the XPS measurement of the LiFePO₄ electrode, the Kaufman-type etching ion source (10 eV, 10 s) was used to eliminate the surface layer on the LiFePO₄. The surface morphology of the samples was observed using SEM (SU-8020, Hitachi).

Preparation of Coin Cells: All the cells were assembled using 2032-type coin cells under a dry Ar atmosphere (H₂O < 1 ppm and O₂ < 1 ppm) in a glove box. Li[FSA] (Kishida Chemical, purity 99%) and DME (Kishida Chemical, purity 99.5%) were mixed to prepare 2 mol dm⁻³ Li[FSA]-DME electrolyte. The positive electrodes were prepared by mixing the active materials (LiFePO₄/C or FePO₄/C) with Super C65 carbon black (MTI) and the single-wall carbon nanotube (SWCNT) dispersed in N-methylpyrrolidone (NMP) with polyvinylidene fluoride (PVDF) (TUBALL) in the weight ratio of LiFePO₄/C (or FePO₄/C):carbon black:SWCNT:PVDF = 91:3:2:4 using a planetary mixer (AR-100, Thinky). The mixture was pasted onto an Al foil and dried overnight at room temperature. The electrode was punched into discs (diameter: 10 mm) and then vacuum-dried overnight at 80 °C to completely remove NMP. The mass loading of the active material was 11–13 mg cm⁻². For the negative electrodes in the CSLMB configuration, lithium metal (Sigma-Aldrich, purity 99.9%) was thinly rolled out, punched (diameter: 10 mm), and crimped onto a Cu current collector, whereas no lithium metal was crimped on a Cu current collector in the LMFB configuration. Electrochemically deposited lithium metal was used to make the CSLMB with the N/P ratio of one. Lithium metal was also served to prepare Cu/Li and Li/Li half cells for the lithium deposition/dissolution tests. A polypropylene separator was used as a separator.

Electrochemical Measurements: The galvanostatic lithium deposition/dissolution tests of the Cu/Li and Li/Li half cells and charge–discharge tests of the CSLMB and LMFB full cells were conducted using a charge–discharge test device (HJ1001SD8, Hokuto Denko) at 25 °C. In the lithium deposition/dissolution tests, lithium deposition and dissolution were alternated every 2 h at 1 mA cm⁻² in the cutoff range of –1.0 and 1.0 V. In the CSLMB and LMFB full-cell tests, the capacity was calculated based on the total weight of the FePO₄ and Li on the positive and negative electrodes. The cutoff voltage was set in the range of 2.0 and 4.0 V. The C-rate was set to 1C = 170 mA (g-LiFePO₄)⁻¹ for Cu/LiFePO₄ cells and 1C = 178 mA (g-FePO₄)⁻¹ for Li/FePO₄ cells to ensure equivalent conditions based on each material's theoretical capacity.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Fumiyasu Nozaki: data curation (lead); formal analysis (lead); funding acquisition (supporting); investigation (lead); resources (lead); visualization (lead); writing—original draft (lead). **Jinkwang Hwang:** conceptualization (equal); formal analysis (equal); funding acquisition (lead); investigation (supporting); methodology (lead); project administration

(lead); supervision (supporting); validation (supporting); writing—original draft (supporting); writing—review & editing (equal). **Kazuhiko Matsumoto**: conceptualization (equal); funding acquisition (equal); project administration (equal); supervision (lead); validation (lead); writing—review & editing (equal).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

FePO₄, Li metal batteries, LiFePO₄, recyclings, sustainabilities

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- [1] a) W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, J.-G. Zhang, *Energy Environ. Sci.* **2014**, 7, 513; b) S. Nanda, A. Gupta, A. Manthiram, *Adv. Energy Mater.* **2021**, 11, 2000804.
- [2] J.-G. Zhang, *Nat. Energy* **2019**, 4, 637.
- [3] a) J. Qian, B. D. Adams, J. Zheng, W. Xu, W. A. Henderson, J. Wang, M. E. Bowden, S. Xu, J. Hu, J.-G. Zhang, *Adv. Funct. Mater.* **2016**, 26, 7094; b) C. Heubner, S. Maletti, H. Auer, J. Hüttel, K. Voigt, O. Lohrberg, K. Nikolowski, M. Partsch, A. Michaelis, *Adv. Funct. Mater.* **2021**, 31, 2106608.
- [4] a) A. A. Assegie, J.-H. Cheng, L.-M. Kuo, W.-N. Su, B.-J. Hwang, *Nanoscale* **2018**, 10, 6125; b) A. A. Assegie, C.-C. Chung, M.-C. Tsai, W.-N. Su, C.-W. Chen, B.-J. Hwang, *Nanoscale* **2019**, 11, 2710; c) C. Cui, C. Yang, N. Eidson, J. Chen, F. Han, L. Chen, C. Luo, P.-F. Wang, X. Fan, C. Wang, *Adv. Mater.* **2020**, 32, 1906427; d) T. T. Beyene, H. K. Bezabh, M. A. Weret, T. M. Hagos, C.-J. Huang, C.-H. Wang, W.-N. Su, H. Dai, B.-J. Hwang, *J. Electrochem. Soc.* **2019**, 166, A1501; e) Z. Yu, P. E. Rudnicki, Z. Zhang, Z. Huang, H. Celik, S. T. Oyakhire, Y. Chen, X. Kong, S. C. Kim, X. Xiao, H. Wang, Y. Zheng, G. A. Kamat, M. S. Kim, S. F. Bent, J. Qin, Y. Cui, Z. Bao, *Nat. Energy* **2022**, 7, 94.
- [5] a) X. Fan, L. Chen, O. Borodin, X. Ji, J. Chen, S. Hou, T. Deng, J. Zheng, C. Yang, S.-C. Liou, K. Amine, K. Xu, C. Wang, *Nat. Nanotechnol.* **2018**, 13, 715; b) F. Qiu, X. Li, H. Deng, D. Wang, X. Mu, P. He, H. Zhou, *Adv. Energy Mater.* **2019**, 9, 1803372; c) C. Niu, D. Liu, J. A. Lochala, C. S. Anderson, X. Cao, M. E. Gross, W. Xu, J.-G. Zhang, M. S. Whittingham, J. Xiao, J. Liu, *Nat. Energy* **2021**, 6, 723; d) D. Wang, J. Qiu, N. Inui, R. Hagiwara, J. Hwang, K. Matsumoto, *ACS Energy Lett.* **2023**, 8, 5248.
- [6] X. Zeng, M. Li, D. Abd El-Hady, W. Alshitari, A. S. Al-Bogami, J. Lu, K. Amine, *Adv. Energy Mater.* **2019**, 9, 1900161.
- [7] M. Shan, C. Dang, K. Meng, Y. Cao, X. Zhu, J. Zhang, G. Xu, M. Zhu, *Mater. Today* **2024**, 73, 130.
- [8] a) Y. Yang, X. Meng, H. Cao, X. Lin, C. Liu, Y. Sun, Y. Zhang, Z. Sun, *Green Chem.* **2018**, 20, 3121; b) B. Gangaja, S. Nair, D. Santhanagopalan, *ACS Sustainable Chem. Eng.* **2021**, 9, 4711; c) H. Jin, J. Zhang, D. Wang, Q. Jing, Y. Chen, C. Wang, *Green Chem.* **2022**, 24, 152.
- [9] a) J. Jiang, W. Shi, J. Zheng, P. Zuo, J. Xiao, X. Chen, W. Xu, J.-G. Zhang, *J. Electrochem. Soc.* **2014**, 161, A336; b) J. Liu, J. Wang, X. Yan, X. Zhang, G. Yang, A. F. Jalbout, R. Wang, *Electrochim. Acta* **2009**, 54, 5656; c) N. Böckenfeld, R. S. Kühnel, S. Passerini, M. Winter, A. Balducci, *J. Power Sources* **2011**, 196, 4136; d) M. Takahashi, H. Ohtsuka, K. Akuto, Y. Sakurai, *J. Electrochem. Soc.* **2005**, 152, A899.
- [10] F. Nozaki, S. Zhang, M. H. Petersen, J. Hwang, J. H. Chang, J. M. García-Lastra, K. Matsumoto, *Energy Environ. Sci.* **2025**, 18, 1408.
- [11] A. S. Andersson, B. Kalska, L. Haggstrom, J. O. Thomas, *Solid State Ionics* **2000**, 130, 41.
- [12] R. Dedryvère, M. Maccario, L. Croguennec, F. Le Cras, C. Delmas, D. Gonbeau, *Chem. Mater.* **2008**, 20, 7164.
- [13] V. Pande, V. Viswanathan, *ACS Energy Lett.* **2019**, 4, 2952.
- [14] S. Wu, T. Wada, H. Shionoya, J. Hwang, K. Matsumoto, R. Hagiwara, *Energy Storage Mater.* **2023**, 61, 102897.
- [15] L. Lin, K. Qin, Q. Zhang, L. Gu, L. Suo, Y.-S. Hu, H. Li, X. Huang, L. Chen, *Angew. Chem., Int. Ed.* **2021**, 60, 8289.
- [16] J. Xiao, Q. Li, Y. Bi, M. Cai, B. Dunn, T. Glossmann, J. Liu, T. Osaka, R. Sugiura, B. Wu, J. Yang, J.-G. Zhang, M. S. Whittingham, *Nat. Energy* **2020**, 5, 561.
- [17] a) C.-J. Huang, B. Thirumalraj, H.-C. Tao, K. N. Shitaw, H. Sutiono, T. T. Hagos, T. T. Beyene, L.-M. Kuo, C.-C. Wang, S.-H. Wu, W.-N. Su, B. J. Hwang, *Nat. Commun.* **2021**, 12, 1452; b) J. Qian, W. A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, J.-G. Zhang, *Nat. Commun.* **2015**, 6, 6362.
- [18] a) M. Cuisinier, J.-F. Martin, N. Dupré, A. Yamada, R. Kanno, D. Guyomard, *Electrochem. Commun.* **2010**, 12, 238; b) M. Cuisinier, J.-F. Martin, N. Dupré, R. Kanno, D. Guyomard, *J. Mater. Chem.* **2011**, 21, 18575.
- [19] a) M. Dubarry, B. Y. Liaw, *J. Power Sources* **2009**, 194, 541; b) P. Liu, J. Wang, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser, P. Finamore, *J. Electrochem. Soc.* **2010**, 157, A499.