Effects of operating temperature on the electrochemical performance of a LiMn_{0.5}Fe_{0.5}PO_4 cathode material for lithium ion batteries

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Abstract. Electrochemical performance of cathode materials for Li-ion batteries depends on their operating conditions, especially temperature. Currently, LiMn_{0.5}Fe_{0.5}PO_4 (LMFP) cathode materials have attracted worldwide attention because of their low cost, low environmental impact, good electrochemical performance and high operating voltage, between 3.5 and 4.1 Volts. We investigated the effects of temperature on the electrochemical properties of LMFP. In this work, LMFP was prepared via a solvothermal method. We evaluated their electrochemical reactions using galvanostatic charge-discharge (GCD) cycling and electrochemical impedance spectroscopy (EIS) at temperatures of 15, 30, and 45 °C. The crystalline structure and morphology of LMFP were characterized using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The results showed that the discharge capacities of LMFP increased with temperature, which corresponded to lower charge transfer resistance within the cell and higher lithium-ion diffusion at elevated temperatures.

1. Introduction
Researchers have done much research to develop new electrode materials for lithium-ion batteries (LIBs), especially cathode materials. Cathode materials play a central role in determining the energy capacity and cost of LIBs [1]. Olivine-based cathode materials (LiMPO_4, where M = Fe, Mn, Co, Ni) such as LiMn_{0.5}Fe_{0.5}PO_4 (LMFP) have combined the good rate capability of LiFePO_4 (~170 mAh/g) and the high potential of LiMnPO_4 (4.1 V vs. Li^+/Li) [2]. Generally, the electrochemical performance of LIBs depends on environmental factors such as temperature and humidity. Many researchers emphasize modifying electrochemical performance at both low (e.g., -20 °C or even lower) and high (e.g., 45 °C or even higher) temperatures. Li et al. [3] discussed the low temperature (~40 °C) performance of a LiFe_{1-x}Mn_xPO_4 composite cathode. They indicated that the charge transfer resistance (Rct) of these composite cathode materials obviously increases when the operating temperature is decreased, especially below -20 °C. Similar results have been found by Liao et al. [4] who studied other olivine cathodes. However, the electrochemical performance at high temperatures is still insufficient. The effects of high temperature on LMFP materials has not yet been reported. This is essential information that is important to operate batteries in tropical countries. Therefore, we investigated the effects of...
environmental temperature (15, 30, and 45 °C) on the electrochemical properties of a LMFP cathode material in the current study.

2. Experiments

2.1. Sample preparation

LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ was synthesized via a solvothermal method. LMFP was prepared at a concentration of 0.125 M with a volume of 50 ml using a ratio of ethylene glycol (EG) solvent to deionized water (DI) of 80%: 20% (volume basis). The precursors of LiOH·H$_2$O (98%; Sigma-Aldrich), MnSO$_4$·H$_2$O (99%; QRëC), FeSO$_4$·7H$_2$O (99.50%; QRëC) and H$_3$PO$_4$ (85%; Ajax Finechem) were mixed in stoichiometric amounts (molar ratio of Li: Mn: Fe: PO$_4$ = 3: 0.33: 0.33: 1). First, LiOH·H$_2$O was dissolved in DI (Solution A) after which MnSO$_4$·H$_2$O and FeSO$_4$·7H$_2$O were dissolved in EG (Solution B). Then, Solution B was well mixed, and a H$_3$PO$_4$ solution was slowly added under continuous stirring to form Solution C. Then, Solution A and Solution C were stirred together under an argon atmosphere for 5 min. The resulting mixture was transferred into a stainless-steel autoclave, followed by a solvothermal treatment at 185 °C for 18 h. After the autoclave was cooled to room temperature, the obtained precipitates were washed several times with DI water until the pH of the solution was neutral. The sample was separated by centrifugation and dried in a vacuum oven at 80 °C for 12 h. LMFP was coated with a sucrose carbon source. The LMFP powder was mixed with 5% (weight basis) sucrose, dissolved in DI water, and then freeze-dried. The mixture was heated at 300 °C for 6 h and 500 °C for 6 h under an argon atmosphere.

2.2. Sample characterization

The crystal structure of the resulting materials was characterized via X-ray diffraction (XRD, D8 Advance; Bruker) using Cu Kα irradiation (λ = 1.54 Å). The XRD patterns were collected over the 20 range of 10-80 degrees. Their morphology was examined using field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450; FEI). Electrochemical impedance spectroscopy (EIS) was performed using an electrochemical analyzer (CS series; CorrTest). An AC voltage of ±5 mV was used over the frequency range of 10$^{-2}$ to 10$^5$ Hz and measured at 15, 30, and 45 °C. The obtained impedance values were fitted using the CS Studio5 program.

2.3. Cathode preparation and cell assembly

For electrochemical testing, the active material was mixed with conductive carbon black (Alfa Aesar) and N-methyl-2-pyrrolidone (NMP; Aldrich) binder mixed with polyvinylidene fluoride (PVDF Kynar 2801; Arkema) at an 80: 9: 1 weight ratio. The mixture was shaken for 2 h 10 min. Then, the resulting slurry was casted onto pure Al foil and dried at 80 °C in a vacuum oven for 12 h. The electrode was assembled in an Ar-filled glovebox as coin-cell type batteries. The coin-cells consist of a cathode material (LMFP), anode material (Li metal), separator (Celgard 2400), and an electrolyte (LiPF$_6$). Galvanostatic cycling tests were performed using a battery analyzer at C/10-5C charge-discharge rates over the voltage range of 2.2-4.6 V vs. Li$/\text{Li}$ at 15, 30, and 45 °C.

3. Results and discussion

We synthesized this material and characterize it to determine temperature effects on its performance. Figure 1(a) shows the XRD patterns of LMFP. It can be seen that the sample was a pure-phase olivine-type LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ crystalline material (PDF#00-042-058). All peaks were indexed according to the $Pmn$$_a$ space group of the orthorhombic structure with lattice parameters of a = 6.0285 Å, b = 10.3586 Å, and c = 4.7031 Å. The results illustrate successful synthesis of a pure LMFP material using the solvothermal method.

The morphology of LMFP material is presented in figure 1(b). FE-SEM images illustrate that the LMFP material consists of highly agglomerated nanoparticles with average sizes of 30-45 nm. The elemental distributions of LMFP were obtained using an energy dispersive X-ray (EDX) technique and
The results are shown in figure 1(c). The LMFP material was composed of Fe, Mn, C, P, and O. Each of the elements was homogeneously distributed in the sample indicating that the sample is single phase.

**Figure 1.** (a) XRD patterns of LMFP, (b) FE-SEM image of LMFP, (c) EDS mapping images of LMFP.

The detailed electrochemical properties of the LMFP material tested at various temperatures are shown in figure 2. The charge-discharge curves of the LMFP material display two typical potential plateaus at about 3.5 and 4.1 V corresponding to the redox potentials of Fe$^{3+}$/Fe$^{2+}$ and Mn$^{3+}$/Mn$^{2+}$, respectively. Figure 2(a) shows the charge-discharge profiles measured at 15, 30, and 45 °C of the LMFP material at a 0.2 C-rate (fully charged or discharged in 2 h). At a 0.2 C-rate, the discharge capacities decreased from 154 mAh g$^{-1}$ to 136 mAh g$^{-1}$, and to 128 mAh g$^{-1}$ when the operating temperatures decreased from 45 to 30 and 15°C, respectively. The charge/discharge profiles demonstrated that a high operating temperature improved the usable capacity of this LMFP material.

**Figure 2.** (a) Typical charge/discharge profiles of LMFP under various operating temperatures; 15 °C (blue line), 30 °C (black line), and 45 °C (red line) at a 0.2 C rate, (b) Nyquist plots of LMFP at various temperatures, (c) temperature dependencies of the various resistances, (d) equivalent circuit model used for EIS fitting.
The Nyquist plots at various temperatures are presented in figure 2(b). According to the literature [3], $R_e$ represented the resistance of the electrolyte, $R_i$ is related to the film resistance at the solid electrolyte interface (SEI), and $R_{ct}$ corresponds to the charge transfer resistance at the electrode/electrolyte interface. The Warburg impedance ($Z_w$) corresponds to the sloping line in the low frequency range and is related to diffusion of Li-ions in the LMFP nanoparticles. The Nyquist plots fitted to an equivalent circuit model are shown in figure 2(d) with impedance parameters are listed in table 1. The values of $R_e$, $R_i$, and $R_{ct}$ tended to decrease as the operating temperature increased. Obviously, the Li-ion diffusion coefficients ($D$), which can be calculated the following equation (1); $R$ is the gas constant, $T$ the absolute temperature, $A$ the surface area of the cathode, $n$ is the number of electrons per molecule attending the electronic transfer reaction, $F$ is Faraday constant, $C$ is the concentration of lithium ion in LMFP electrode, $\sigma$ is the Warburg factor which has the relationship with $Z_w$ [5]. From calculating, $D$ increased with increasing temperatures. Figure 2(c) shows the relationship between resistances and temperatures. The $R_{ct}$ significantly decreased with increasing temperature while the $R_e$ and $R_i$ varied slightly with operating temperatures. The results indicate that the improved electrochemical performance of the LMFP material at high operating temperatures is due to the reduction of all resistances and increased Li-ion diffusion coefficients.

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$

### Table 1. Resistances and diffusion coefficients fitted by the equivalent electric circuit.

| Temperatures (°C) | $R_e$(Ω) | $R_i$(Ω) | $R_{ct}$(Ω) | $D$(cm$^2$s$^{-1}$) |
|-------------------|----------|----------|-------------|-------------------|
| 15                | 5.54     | 93.98    | 232.85      | 8.51×10$^{-12}$   |
| 30                | 2.89     | 35.84    | 130.21      | 1.42×10$^{-11}$   |
| 45                | 3.99     | 7.10     | 69.08       | 2.20×10$^{-11}$   |

### 4. Conclusions

Electrochemical properties of a LMFP cathode material at high operating temperatures have been investigated. The results indicate that a high operating temperature improved the usable capacity of the LMFP material. The EIS results clearly show that Li-ion diffusion coefficients increased with operating temperatures. The overall resistances all decreased with increased operating temperatures. The results show that the improved electrochemical performance of LMFP with increased temperatures was due to lower charge transfer resistances within the cell and higher lithium-ion diffusion at elevated temperatures. Various weather conditions produced different electrochemical performance in lithium-ion batteries. Therefore, this study provides useful information for Li-ion batteries which are used in tropical countries such as Thailand.

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