



Short communication

Evaluation of lithium ion cells with titanate negative electrodes and iron phosphate positive electrode for start–stop applications



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HIGHLIGHTS

- Investigated the dependence of an LFP/LTO cell energy density on rate and temperature.
- Indicated that improving electrolyte kinetics is the key to enhance low temperature power.
- Pulse cycle tests showed excellent life performance with minimal capacity loss.
- We modeled the circuit parameters of LFP/LTO cell using cyclic voltammetry data.
- Circuit model results indicated the circuit parameters have little SOC dependence.

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ABSTRACT

Start–stop systems require the battery to provide high power, endure shallow cycling, and exhibit long cycle life. The LFP/LTO (lithium iron phosphate/lithium titanate) battery is a potential candidate to meet such requirements because, at room temperature, both materials can be operated at high rate and have good stability (calendar and cycle life). In this work, we have investigated the feasibility of using Li_xFePO₄/Li_{4+3y}Ti₅O₁₂ ($0 < x < 1$, $0 < y < 1$) lithium ion batteries for start–stop systems. We evaluate both the rate and temperature dependence of LFP/LTO cells subjected to galvanostatic charge/discharge cycling. Excellent rate performance was observed at temperatures above or at ambient. However, at low temperatures, significant resistance is observed, and this must be addressed for the LFP/LTO system to be viable. In addition, we investigate the SOC dependence of equivalent circuit parameters using triangular current and voltage excitation method to facilitate the implementation of circuit-based control algorithms for vehicle applications. Parameter values are nearly constant over the broad voltage-plateau region of the substantially two-phase behavior of both the LFP and LTO materials.

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1. Introduction

Implementation of start–stop systems is a pragmatic approach for reducing vehicle fuel consumption. During start–stop operation, the engine automatically shuts down when the vehicle comes to a stop and then quickly restarts when propulsion is desired by the operator.¹ Such start–stop operations of the vehicle

can effectively reduce the amount of engine idling time, leading to fuel savings and reducing unwanted emission. Lead-acid batteries are used today for high-volume start–stop vehicle offerings because lead-acid batteries have good low-temperature specific power (kW kg^{−1}) and low initial cost [1]. Frequent high discharge rates can significantly reduce the life of lead acid batteries [2], which motivates the identification of an alternative battery system.

Lithium ion batteries are the leading candidates for automobile applications providing that there are challenges from the cost, and safety perspectives. [3–5] Because of their high specific power and long (cycle and calendar) life, lithium ion batteries are very appealing for power assist vehicular applications. Particularly, Li-ion batteries combining Li_xFePO₄ (LFP, $0 < x < 1$) as the positive

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¹ Typical start–stop systems are designed such that the engine is off when the brake pedal is depressed and the vehicle is stopped. When the operator removes pressure on the brake pedal, the engine starts.

electrode material and a $\text{Li}_{4+3y}\text{Ti}_5\text{O}_{12}$ (LTO, $0 < y < 1$), as the negative electrode material, can provide significantly improved cycle life, and superior power capability [6]. Both LFP [7–14] and LTO [6,15–17] are known to provide excellent cycle life and rate capability. More importantly, recent developments in nano-engineering of electrode materials significantly improved power capability of lithium ion technology. [13,14,18] Zaghbi et al. recently [6] demonstrated that LFP/LTO in an 18650 format cell offers excellent charge/discharge rate capabilities and long life. Hence, the LFP/LTO battery is a promising candidate to meet start–stop requirements.

In this work, we evaluate the feasibility of a commercial grade 18650 LFP/LTO cell using electrochemical methods. First, the rate capabilities of the LFP/LTO cell are investigated using galvanostatic charging and discharging at different temperatures between -30 and 45 °C. The rate performance at high temperatures was excellent while significant resistance rise was observed at low temperatures. Further examination of the temperature dependence of the resistance using the Arrhenius relation suggests the electrolyte resistance limits the cell performance at low temperatures. Further, the cold cranking power is evaluated at -30 °C. We also employ a pulse cycling protocol to examine the long term cycling stability of LFP/LTO. The results are very promising with very minimal capacity and power degradation. Last, we employ a model incorporating electrical circuit elements to correlate the cell behavior. The circuit-element parameters are then regressed from cyclic voltammetry data. Results indicate the circuit parameters (R , R_{ct} , and C) have little SOC dependence. Overall, the LFP/LTO system is a potential candidate for meeting all the requirements for start–stop applications, although a suitable electrolyte composition is needed to improve the low temperature performance.

2. Experimental

2.1. Materials and characterization methods

Commercial grade 18650 cells were prepared that composed of carbon coated LiFePO_4 cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. The details of materials synthesis and cell fabrication were published elsewhere. [3] Briefly, LiFePO_4 was synthesized through a carbonthermal process using iron and EBN-1010 graphite power as a reducing agent at 1050 °C for 5 min, then used jet-mill and wet-mill in isopropyl alcohol solution process to reduce the particle size to nanoscale. Followed by carbon coating process by mixing the lactose carbon precursor in aqueous solution and heated the final product at 700 °C for 4 h to achieve 2 wt% C LiFePO_4 . LiFePO_4 cathode electrode was made from slurry consisting of 90 wt% of LiFePO_4 , 6 wt% of carbon black, 2 wt% of CMC and 2 wt% of WSB by using water solvent. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material was prepared by solid-state reaction of precursor materials TiO_2 and Li_2CO_3 and carbon heated at 850 °C for 18 h. A standard commercial electrolyte of 1 M LiPF_6 in EC/DEC was used for the cell fabrication. Capacity characterizations were performed at different temperatures and rates. The tests were conducted using a MACCOR tester (Series 4000). The cells were fully charged to 2.5 V, followed by a voltage hold, and then discharged to 0.5 V. The cell is rated as 1 Ah; therefore, 1 C rate is defined as a constant-current magnitude of 1 A. For Hybrid Pulse Power Characterization (HPPC) tests, taken at every 10% SOC after resting for 1 h, we applied a pulse power sequence which composed of three steps: (1) 5 C charge for 10 s, (2) rest at OCV for 40 s, and (3) 5 C discharge for 10 s. For all the electrochemical testing, a TestEquity environmental chamber (Model 107) was used for the temperature control. Cold cranking tests consist of 2 s discharge and charge pulses at -30 °C and at 30% SOC. Two-second

voltage holds at 1.0 V and 2.5 V were applied 3 times with 10 s intervals between each pulse for maximum discharge and charge power determinations, respectively. Long term pulse power cycling stability test was performed using a prescribed profile: (1) discharge for 59 s at 1 C rate, (2) discharge 1 s at 5 C rate, (3) charge 32 s at 2 C rate, and (4) rest for 28 s. The cell was continuously cycled under the prescribed pulse power profile at room temperature. Periodically, the test was interrupted for a C/10 capacity characterization.

The cyclic voltammetry (CV) experiments were carried out using a PAR EG&G 283 potentiostat. Starting at a fully charged state, the cell was discharged at 1 C rate to 80% SOC with a rest of 1 hr. Then the voltage was scanned between ± 15 mV against the OCV at various rates from 50 to 0.5 mV s^{-1} . The experiments were then repeated for 60, 40, and 20% SOC.

3. Results and discussion

3.1. Electrochemical evaluation

Fig. 1 shows the voltage profile of the LFP/LTO cell subject to galvanostatic charge/discharge at C/2, 2 C, and 5 C rates and at temperatures of -20 , 0, 25, and 45 °C. The rate and temperature dependence of the cell capacities are summarized in Fig. 2. The rate capabilities of LFP/LTO cell are excellent at or above room temperature (25 °C). Even at a 5 C rate at 25 °C, the cell maintains 99% of its full capacity. However, as temperature decreases to below 0 °C, we observe an increase in voltage hysteresis between charge and discharge, a clear indication of resistance rise. At -30 °C, capacity retention was about 20–30% of the value at ambient temperatures, even at modest charge/discharge rates (below 2 C rates). The slight increase in capacities in going from 2 to 5 C rates at -20 and 0 °C were a result of improved kinetics due to internal heating at high rates.

We further examined the temperature effects on resistance using HPPC. Fig. 3 shows the discharge and charge resistances plotted as a function of depth of discharge (DOD) at -20 , 0, 25, 35, and 45 °C. For the purposes of Fig. 3, discharge and charge resistances were determined using a $\Delta V/\Delta I$ calculation method from pulse power characterizations. The discharge resistance at each specific SOC was calculated from voltage change, ΔV of a constant current discharge pulse divided by the current applied, ΔI at the pulse duration. Similarly, the charge resistance, or regenerative resistance at each SOC was calculated from of a constant current charge pulse divided by the current applied, ΔI at the pulse duration. The details of the calculation procedures can be found elsewhere [19]. It is evident that the resistance increased more significantly at low temperatures (Fig. 3). Arrhenius plots were also constructed for the resistance at 20% DOD in Fig. 4. We observed two distinct linear Arrhenius relation regions and the activation energy were calculated from the slope of the curves from each region. At temperatures below ambient, the activation energy was estimated at 25 kJ mol^{-1} as compared to only 4 kJ mol^{-1} for the region above ambient. In the low temperature region, the activation energy is similar to the value for the electrolyte indicating that the resistance is dominated by the electrolyte. At higher temperatures, very low activation energy suggests the resistance is no longer limited by the electrolyte; solid-phase resistances are often less temperature dependent than those of liquid electrolytes [20], and the higher-temperature results are consistent with the solid-phase resistance dominating at elevated temperatures. Thus, the results are consistent with the assertion that resistance of electrolyte is responsible for the high resistance of the cell at low temperatures.

We have also investigated the cold cranking power capability at -30 °C. The cell was tested at 30% SOC with three 2 s voltage

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