

Optimization of Inactive Material Content in Lithium Iron Phosphate Electrodes for High Power Applications



Seonbaek Ha^{a,*}, Vijay K. Ramani^a, Wenquan Lu^{b,**}, Jai Prakash^{a,*}

^a Department of Chemical and Biological Engineering, Center for Electrochemical Science and Engineering, Illinois Institute of Technology, 10 West 33rd Street, Chicago, IL 60616, United States

^b Electrochemical Energy Storage, Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Building 200, Argonne, IL 60439-4837, United States

ARTICLE INFO

Article history:

Received 30 October 2015
Received in revised form 23 December 2015
Accepted 7 January 2016
Available online 8 January 2016

Keywords:

LiFePO₄
electrode optimization
four-point probe conductivity
area specific impedance
lithium ion batteries

ABSTRACT

The electrochemical performance of lithium iron phosphate (LiFePO₄) electrodes has been studied to find the optimum content of inactive materials (carbon black + polyvinylidene difluoride [PVDF] polymer binder) and to better understand electrode performance with variation in electrode composition. Trade-offs between inactive material content and electrochemical performance have been characterized in terms of electrical resistance, rate-capability, area-specific impedance (ASI), pulse-power characterization, and energy density calculations. The ASI and electrical conductivity were found to correlate well with ohmic polarization. The results showed that a 80:10:10 (active material: binder: carbon agents) electrode had a higher pulse-power density and energy density at rates above 1C as compared to 90:5:5, 86:7:7 and 70:15:15 formulations, while the 70:15:15 electrode had the highest electrical conductivity of 0.79 S cm⁻¹. A CB/PVDF ratio of ca. 1.22 was found to be the optimum formulation of inactive material when the LiFePO₄ composition was 80 wt%.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The use of lithium iron phosphate (LiFePO₄) as the positive electrode in a lithium-ion battery has been extensively investigated due to its low toxicity, low cost, long cyclability, good thermal stability, and relatively high theoretical specific capacity of 170 mAh g⁻¹ [1–3]. However, the LiFePO₄ electrode has poor rate capability at higher currents due to the low electronic conductivity of LiFePO₄ (10⁻⁹ S cm⁻¹) [4]. There have been previous efforts to improve the electrochemical performance of the LiFePO₄ using methods such as carbon coating [5–10], controlling particle size [11–13], and metal doping [4,14]. Prior work has also addressed the importance of the composition of the electrode material and the correlation between the electrode's physical properties (extrinsic) and electrochemical properties. The latter work involved the study of engineering approaches towards electrode fabrication for better electrochemical performance. Zaghbi et al. studied the influence of

carbon source (carbon black and graphite) when mixed with 12 wt % of polyvinylidene difluoride (PVDF) on the performance of a LiFePO₄/C (~1 wt% of carbon coated) electrode using measurements of gravimetric/volumetric capacity variation, rate capability, and cyclic performance [15]. Liu et al. reported the electrical conductivity of acetylene black (AB)/PVDF binder film and the electrochemical performance variation of the LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode (PVDF: AB = 2:1, 1.25:1, 1:1) [16]. Chen et al. focused on how the electrode's conductivity and the void fraction of the electrode matrix could be related to carbon obtained from different sources by performing packing simulations [17]. The electrode's porosity and thickness were found to be important factors that affected electrochemical performance. Their system was characterized by using area-specific impedance (ASI), electrochemical impedance spectroscopy measurements (EIS) and hybrid pulse power characterization (HPPCs) [18,19]. Generally, it has been established that adding carbon to a bare LiFePO₄ electrode leads to better rate capability and/or better electrochemical performance because of higher effective conductivity and utilization of active material. However, increasing the amount of inactive materials will reduce the volumetric capacity, energy density, and power density.

The electrode optimization study of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ [19–21] and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ [16,22–24] cathode material has

* Corresponding authors. Tel.: +1 312 567 3639; fax: +1 312 567 8874.

** Corresponding author. Tel.: +1 630 252 3704; fax: +1 630 972 4414.

E-mail addresses: sha5@hawk.iit.edu (S. Ha), wenquan.lu@anl.gov (W. Lu), prakash@iit.edu (J. Prakash).

been performed. There have been several studies to investigate the electrochemical behavior of LiFePO_4/C and bare LiFePO_4 when coupled with inactive materials. LiFePO_4/C composite materials had been synthesized by using different carbon sources [15,25,26]. Zheng et al. studied the thickness effect of a LiFePO_4 (80.8:7.2:12 = LiFePO_4 :AB:PVDF) electrode [19]. Bommel et al. revealed the calendaring effect on LiFePO_4 electrode (90:5:5) [27]. (A calendaring process is a typical step in the electrode fabrication process for lithium-ion batteries. This step improves the electrochemical performance due to the enhancement of the contact between the electrode materials in the electrode matrix as well as contact between the electrode materials and current collector [18,27,28]). Due to the complex and porous structure of the electrode, a comprehensive understanding of the relationship between the electrode composition, electrical conductivity, power and/or energy density, and rate capability is required to acquire optimum electrode performance for practical applications such as in electric vehicles (EVs) and plug-in hybrid electrical vehicles (PHEVs) [29,30].

To the best of our knowledge, mapping of LiFePO_4 electrode compositions and factors such as electrical conductivity and loading level on electrochemical performance has not been specifically discussed in previous studies [15,19]. In our study, the goal was to find the optimum component composition within the electrode and to investigate major factors influencing the performance in a bare LiFePO_4 electrode. We have investigated how electrical conductivity affects the electrochemical performance. Electrical conductivity, overvoltage, ASI, specific capacity, pulse-power density, and energy density of the electrodes were all systematically examined by changing the active material mass fraction with an identical carbon black (CB)/PVDF ratio and by changing the CB/PVDF ratio with a fixed LiFePO_4 mass fraction.

2. Experimental

2.1. Electrode preparation

Preparation of the LiFePO_4 electrode includes slurry fabrication, casting, and drying. LiFePO_4 (obtained from Aleees Inc.), carbon black (Super P[®], obtained from Timcal), KF 1120 (PVDF binder; obtained from Kureha) and N-Methylpyrrolidone [NMP, obtained from Sigma–Aldrich] were used as electrode precursor materials. 12 wt% of KF 1120 was dissolved in NMP solution. The amount (5 g) of LiFePO_4 was fixed in all slurries while the PVDF and carbon black amounts were changed by a targeted ratio. Initially, the active material and carbon black powder were mixed, and then the KF 1120 solution with additional NMP solution was added to these powders to get homogenous slurries. NMP was initially added to target $\sim 35 \pm 5\%$ of solid in the total slurry amount: (solid/(solid + liquid)) $\approx 0.35 \pm 0.05$, solid = active material + carbon black + 12 wt% of KF1120 solution, liquid = 88 wt% of KF 1120 solution + additional NMP). The premixed LiFePO_4 /Super P/PVDF was well dispersed using a planetary centrifugal mixer (THINKY Mixer). The slurries were casted onto an aluminum (Al) foil (20 μm thick) using a doctor blade. The laminate thickness was controlled by adjusting the doctor blade height (75–225 μm , 25 μm intervals). Casted laminates were dried in an oven set at 75 °C for 4 hours and dried again at 75 °C in a vacuum oven overnight. All laminates were punched into 9/16 in. diameter disk electrodes and dried again at 120 °C for at least 4 h in a vacuum oven inside an argon-filled glove box. Dried electrodes (uncalendered) were assembled in a CR2032-type coin cell as a half-cell with a lithium metal counter electrode (9/16 in. diameter disk) and a Celgard[®] 2325 separator (5/8 in. diameter disk). The electrolyte used was 1.2 M LiPF_6 with ethylene carbonate (EC)/ethyl methyl carbonate (EMC), 3/7 by weight.

2.2. Electrical conductivity measurements

All slurries were also coated onto non-conducting, transparent films by using identical doctor blade methods. The electrical conductivity of these laminates (uncalendered) was measured by using the four-point dc probe method [31]. A Keithley 2400 Source Meter[®] combined with a Lucas 302 resistivity stand was used for these measurements. Laminate (or electrode) thickness was measured by a Mitutoyo Digital Plunge Indicator (ID-C112TB).

2.3. Electrochemical characterization

All electrodes were cycled for three formation cycles at a C/20 rate using a Maccor series 4000 cell cycler at room temperature, before further electrochemical performance tests. The operating voltage window applied to the Li/ LiFePO_4 half-cells was 2.5–4.0 V (vs. Li/Li⁺). After three formation cycles, a rate capability test was performed with a constant charging current of 0.1C and different discharge rates (0.1C, 0.2C, 0.3C, 0.5C, 1C, 2C, 3C, and 4C). The cell was held at the upper cutoff voltage (4.0V), until the charging current dropped to C/20 during the rate capability test.

After the rate capability test, the hybrid pulse power characterization (HPPC) test [29,30] was conducted on all cells. A 3C discharge pulse for 10 s and a 2C regenerative charge pulse for 10 s were applied to the cells, with a 40 s rest interval between the discharge pulse and the regeneration pulse. The pulse profiles were performed at 10% DOD intervals from 10% to 90% of depth of discharge (DOD). The area-specific impedance (ASI) was calculated from the voltage change before and at the end of the discharge pulse.

3. Results and Discussion

Fig. 1 shows electrode thickness and active material (AM) loading as a function of AM mass fraction with fixed CB/PVDF ratio (CB:PVDF = 1:1). Experimentally, attempts were made to obtain approximately identical active loadings on the order of 3.6–3.7 mg cm^{-2} by using gap separation of lab-scale doctor blades. This

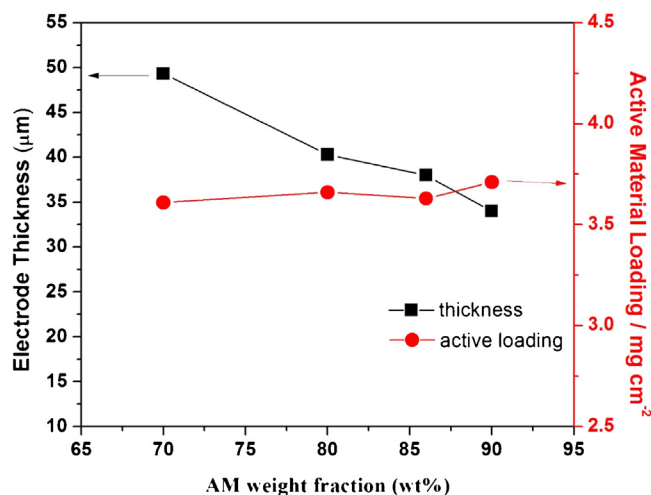


Fig. 1. Average thickness (non-calendered) and active material loading of all electrodes as a function of LiFePO_4 active material (AM) weight fractions (AM:CB:PVDF = 90:5:5, 86:7:7, 80:10:10, and 70:15:15); Al foil weight and thickness were excluded.

Download English Version:

<https://daneshyari.com/en/article/6608960>

Download Persian Version:

<https://daneshyari.com/article/6608960>

[Daneshyari.com](https://daneshyari.com)