Journal of Manufacturing Processes 20 (2015) 198–205

Contents lists available at ScienceDirect

Journal of Manufacturing Processes

journal homepage: www.elsevier.com/locate/manpro

Fabrication of rechargeable lithium ion batteries using water-based inkjet printed cathodes

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ARTICLE INFO

Article history:
Received 20 March 2015
Received in revised form 14 July 2015
Accepted 3 August 2015
Available online 21 August 2015

Keywords:
Thin film
Ink-jet printing
Energy storage
Current collector

ABSTRACT

Water soluble $LiFePO_4$ inks for lithium ion battery cathodes were prepared and characterized. The pH versus aging time plot shows that stable inks have pH values around 9.13. Inductively Coupled Plasma (ICP) and X-ray Diffraction (XRD) results indicate that impurities are generated as the pH reaches its stable value. Electrical conductivity measurements however suggest that non-electrochemically active impurities lower the electrical conductivity of $LiFePO_4$. A $LiFePO_4$ particle size change due to different binder adsorption mechanisms on the carbon surface is caused by changes in ion concentration which is determined by the initial pH values. Electrodes are fabricated by inkjet printing using ink prepared with an initial pH of 9.13 on two current collectors (aluminum foil and carbon nanotube paper (CNT paper)). A clear boundary between the aluminum current collector and electrode materials was observed using Scanning Electron Microscopy (SEM), which is possibly caused by the reaction between the alkaline dispersing solvent and the Al foil. XRD results also suggest the existence of impurities like $LiAlO_2$ and $AlPO_4$ after inkjet printing. Despite the uniform morphology of the electrode, electrochemical performance is still poor due to the impurities between the Al current collector and active materials. In contrast, a strong connects between active materials and CNT paper was confirmed by SEM. Battery with CNT paper current collector exhibited better electrochemical performance than Al current collector. This indicates that CNT paper is an alternative to the Al-foil current collector for $LiFePO_4$ aqueous based ink.

1. Introduction

$LiFePO_4$ cathode material has received more attention in recent years due to less toxicity, lower cost and higher thermal stability properties [1]. Although it has low lithium ion conductivity especially at high charge–discharge rates, more and more technologies have been developed to solve this problem [2–5]. The current $LiFePO_4$ cathode materials employ chemically toxic materials (polyvinylidene fluoride (PVDF) as a binder and organic solvents (e.g., NMP) as solvent) for the electrode preparation process. It is required to alleviate the environmental pollution during the electrode preparation by replacing the organic system slurry with an aqueous formulation [6]. Considering the insolubility of PVDF in water, other alternatives are needed. In this context, sodium carboxymethyl cellulose (SCMC) is a good non-fluorinated binder candidate since it has been widely used in anode electrodes for lithium-ion batteries [7]. SCMC can be easily dissolved in water and has significant advantages compared with the PVDF/organic system: (a) low cost and (b) environmentally green. Some groups reported that SCMC-based electrodes showed even high packing density due to the substantial shrinkage of cellulose during the drying step. In addition, SCMC based electrode with high packing density can further increase the contact between active materials and conductive agent thereby contribute to the improvement of the electrochemical properties of the electrode as well as mechanical properties of electrodes [8]. Replacing the PVDF binder with SCMC yields superior coulombic efficiency and specific capacity with charging/discharging cycling [9,10] and also improves the rate at which the battery can be recharged. Since SCMC is a non-fluorinated binder, it will not produce fluorinated degradation products (At elevated temperatures, PVDF reacts with LiC_6 to form LiF and some —(—C═C—F)— species via an exothermic reaction which causes a risk for the onset of thermal runaway) [6,9,10]. It is required to develop the electrode material prepared by a water-based green process to fabricate the $LiFePO_4$ cathode.

On the other hand, inkjet printing, at first, was used as a text/graphic processing method [11]. Inkjet printing's drop-on-demand feature enables patterned deposition of materials on

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http://dx.doi.org/10.1016/j.jmapro.2015.08.003
1526-6125/

different types of substrate in a fast and economic way. Consequently, inkjet printing became one of the most promising rapid thin film manufacturing techniques compared to conventional film fabrication methods such as spin coating, screen printing, painting [12] and stencil printing. Metallic, polymer and bio materials are examples which can be successfully printed by inkjet printing methods [13,14]. For the cathode materials, thin films of both primary (i.e. disposable) batteries and secondary (i.e. rechargeable) cathode materials have been fabricated by inkjet printing methods. Xu et al. have used inkjet printing method to prepare thin film MnO_2 electrodes (1.4 μm in thickness) for alkaline Zn–MnO_2 batteries [15]. The fabricated MnO_2 electrode demonstrated an outstanding energy capacity at high discharge rate (270 mA h g^{-1} at 14.4 C). Their study also shows that inkjet printing could improve the active material distribution state and avoid agglomeration on the collector.

In this study, we examined the physical and chemical properties of $LiFePO_4$ ink with different initial pH values. In addition, the electrochemical performances of the $LiFePO_4$ electrode fabricated by ink-jet printing were investigated.

2. Experimental procedure

2.1. $LiFePO_4$ ink and electrode preparation

Commercial $LiFePO_4$/C powder, carbon black and SCMC from Sigma Aldrich were used as cathode materials, conductive agent and binder, respectively. Inks were made following the ratio $LiFePO_4$:CB:SCMC = 8:1:1. The mixed powder was added into different pH solutions adjusted by HCl and NaOH for five different solutions: pH 3, 5, 7, 9 and 10 named samples A, B, C, D and E. The mass fraction of solid in suspension was 5 wt% with triton X-100 as the surfactent. After 30 min bath sonication, each suspension was centrifuged for 10 min at 4000 rpm to move the possible big particles. Glycerin was added to the ink to make the final viscosity around 13 cp (recommended by the inkjet printer). Each ink was then transferred into a cartridge and printed using Dimatix-2800 inkjet printer (Fujifilm Dimatix Inc.). Aluminum foil and carbon nanotubes (CNT) micro-paper were used as current collectors. The printed electrodes were dried in vacuum at 300 °C for 2 h to evaporate solvent including glycerin. Eventually, electrode, lithium metal foil (anode) and separator (Celgard 2400) were assembled into R2032 button cells in an argon-filled glove box with $LiPF_6$ (1 M) in a 1:1(v/v) mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) is used as electrolyte. Regular electrodes (marked as regular) were also fabricated as a comparison by tape casting using PVDF as the binder.

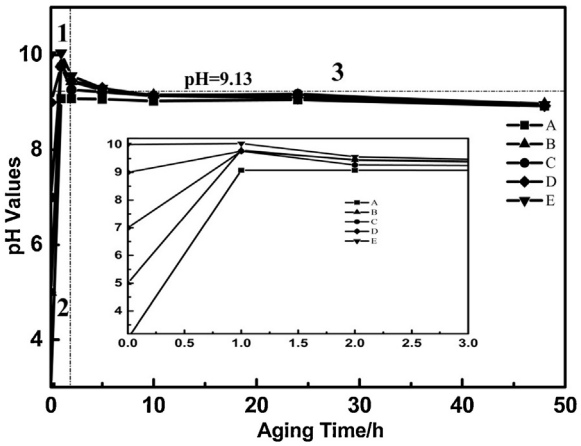

Fig. 1. pH values as a function of aging time of inks and details of pH change in the first 3 h.

2.2. Physical characterization

X-ray diffraction (XRD) measurements were carried out on a Philips PW3040 X-ray Diffractometer, 2θ ranges from 10° to 90° with CuK_α radiation (λ = 15.4 nm) with a step size of 0.02° and a time per step of 15 s. LEO 1530VP Field Emission Scanning Electron Microscope (SEM) was used to examine surface morphology of electrodes. Ionic concentration was measured by (Agilent 7500i Benchtop) Inductively Coupled Plasma-Mass Spectrometer System (ICP-MS). The particle size and size distribution in the solution was recorded by Laser Diffraction Particle Size Analyzer (Beckman Coulter LS230).

2.3. Electrochemical characterization

Dimatix-2800 is used to fabricate electrodes where the computer controlled inkjet printer head is mechanically positioned over a movable platen fabricates the desired pattern.

Coin-type half cells are cycled at a rate of 0.1 C (1 C = 150 mA h g^{-1}) between 2.0 and 4.0 V at 25 °C, using a Battery Analyzer (BST8-MA, MTI Inc.). The cyclic voltammetry (CV) measurements were carried out on CHI832C (CH Instruments, Inc.) at 25 °C.

3. Results and discussion

Fig. 1 shows the pH values' evolution of inks as a function of aging time and details of pH change before the first 3 h. It is

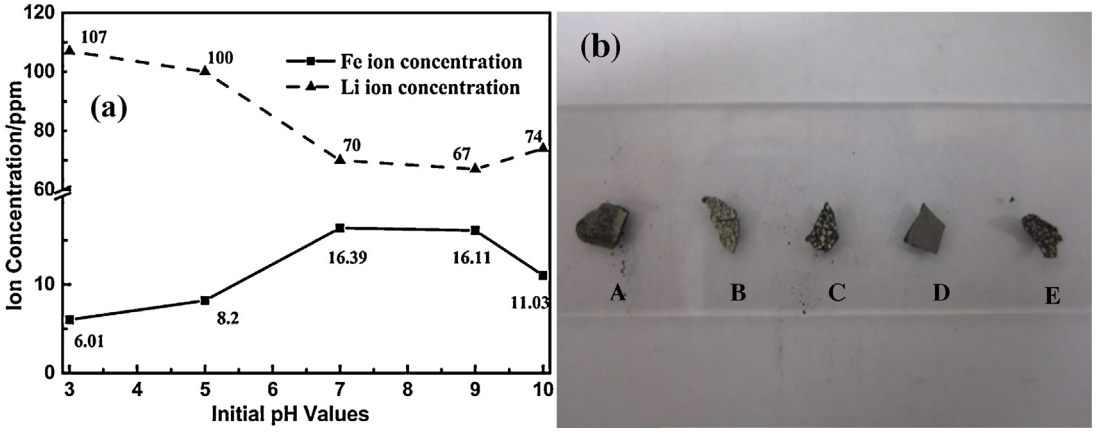

Fig. 2. (a) Ion concentration with different initial pH values after 48 h; and (b) Optical images of particles from dried inks (powder).