Journal of Power Sources 287 (2015) 261–268

Contents lists available at ScienceDirect

Journal of Power Sources

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

Ink-jet printed porous composite $LiFePO_4$ electrode from aqueous suspension for microbatteries

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HIGHLIGHTS

- Rheological study of $LiFePO_4$ aqueous suspensions for piezoelectric ink-jet printer.
- Study of electrochemical behavior of ink-jet printed $LiFePO_4$ porous microelectrodes.
- These microelectrodes show very high power and cyclability with liquid electrolytes.
- Toward fast and cost-effective ink-jet printing of lithium microbatteries.

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form
26 March 2015
Accepted 13 April 2015
Available online

Keywords:
Microbattery
Ink-jet printing
Electrode
Formulation
$LiFePO_4$

ABSTRACT

This work demonstrates ink-jet printed $LiFePO_4$-based composite porous electrodes for microbattery application. As binder and dispersant, we found that aqueous inks with more suitable rheological properties with respect to ink-jet printing are prepared with the low molecular weight poly-acrylic-co-maleic acid copolymer, rather than with the carboxymethyl cellulose standard binder of the lithium-ion technology. The ink-jet printed thin and porous electrode shows very high rate charge/discharge behavior, both in $LiPF_6$/ethylene carbonate-dimethyl carbonate (LP30) and lithium bis(trifluoromethane) sulfonylimide salt (Li-TFSI) in N-methyl-N-propylpyrrolidinium bis(trifluoromethane)suflonylimide ionic liquid (PYR13-TFSI) electrolytes, as well as good cyclability.

1. Introduction

Lithium batteries are actually good solutions to answer increasing energy storage needs of our societies especially for mobile applications (computer, cell phone, EV, …). Many improvements are focused on improved batteries in order to have a massive development of electric vehicles and storage of renewable energies: higher voltage at the positive electrode, higher capacity at both electrodes, longer cycle life, cheaper active material, safer electrolyte. Nevertheless there is an important demand, needing significant developments, for microsources of energy, i.e. microbatteries [1,2]. Many applications, like active radio-frequency identification (RFID), autonomous sensors network, smart cards, implanted medical or pharmaceutical devices etc, [3] require a microbattery as powering sources indeed, with surface about mm^2 to cm^2 with less than mm thickness, with capacity from μAh to mAh and all solid state design.

Developed in first by Kanehori [4], microbatteries are usually fabricated through vacuum-based process such as Physical Vapor Deposition (PVD) of dense layers (electrodes and electrolyte). Typically LiPON is used as solid state electrolyte [5,6], $LiCoO_2$ as positive electrode and lithium metal as negative electrode. This fabrication technology seems too expensive and too slow for mass-commercialization of microbatteries, so it is worth developing a different way to produce microbatteries than vacuum-based process. Several promising researches are focused in this way and on wet process deposition particularly. Wet deposition process like spray, ink-jet or screen printing should allow cost reduction for the fabrication of microbatteries because the equipments are much cheaper than high vacuum deposition techniques and deposition

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http://dx.doi.org/10.1016/j.jpowsour.2015.04.067

rates are much faster [7]. Furthermore, wet process can deposit already crystallized material directly without post-annealing treatment such as sintering by using suspensions of solid particles in a solvent. So aerosol deposition succeeded to deposit $LiFePO_4$ positive electrode [8] with 745 nm thickness and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ negative electrode [9] with controlled thickness from less than 5–40 μm. Also screen printing process was used to obtain $LiCoO_2$ positive electrode for microbattery [10–13]. We have also noted drop-on-demand ink-jet printing process to fabricate $LiCoO_2$ based positive electrode [14–16] using simple office printer for the deposition. More recently, 3D interdigitated electrodes for microbattery [17] were realized after sintering inks deposited thanks to syringe with flow controlled by air pressure.

Subsequently, our strategy is to develop low cost ink-jet printed microbatteries with solid electrolyte and porous composite electrode for microelectronic technology. Our previous work presents ink-jet printing of an ionogel [18] as a solid electrolyte, compatible with porous composite electrodes [19]. This present study is focused on formulation of an ink of a $LiFePO_4$-based positive electrode for piezoelectric ink-jet printer. The electrochemical performances of the printed electrodes are then studied but using standard liquid electrolytes.

Ink-jet printing is basically a simple way for deposition: drops of an ink are ejected through piezoelectric nozzles, reach the substrate and form expected film layer after solvent evaporation. Drop jettability results from the complex combination of inertial, viscous, and surface tension forces, which depend on intrinsic properties of the ink, such as density, viscosity and surface tension, and on extrinsic parameters such as the nozzles diameter, the voltage waveform, etc [20]. The rheological properties of the ink are likely to be the most critical. Improperly formulated inks cannot be ejected, or can deposit in undesired locations, degrading pattern integrity, or can cause nozzle clogging, etc.

2. Experimental

2.1. Materials

Positive electrodes are developed with carbon-coated $LiFePO_4$ (lithiated iron phosphate).

This $LiFePO_4$ has a carbon content of about 3 wt%, and a specific surface of 20 $m^2.g^{-1}$. The size of the primary particles is in the 60–100 nm range. The carbon black chosen as conductive additive is a Carbon Super P™ (C_{SP}) from Timcal with a specific surface of 60 $m^2.g^{-1}$, with primary spherical particles from 10 nm to 90 nm. These particles are fused together in the form of aggregates with a 100–300 nm mean diameter. Different complementary additives are evaluated for the aqueous electrode formulation: the carboxymethyl cellulose (CMC) (from Sigma–Aldrich with 0.7 mol carboxyl per mol cellulose and a molar mass of 250,000 g mol^{-1}) that can be used as a binder for positive electrode [21–26], the isooctylphenylether of polyoxyethylene (Triton X-100 from Aldrich, $M = 652$ g mol^{-1}) that can be used as a surfactant to disperse C_{SP} in water [27–30], the poly-acrylic-co-maleic acid (PAMA from Sigma–Aldrich $M = 3000$ g mol^{-1}) with a low molecular weight polymer that can be used as a dispersant as well as binder [31,32] for $LiFePO_4$ and C_{sp} [33].

2.2. Preparation of the composite electrode

Different inks are prepared from these materials with a solid fraction of 10 wt%. Each suspension contains the active material ($LiFePO_4$), the electronic conductor (C_{SP}) and one or several complementary additive(s), i.e. CMC, TX100, PAMA. The different components are dispersed in water by magnetic stirring for 12 h and a further ball milling for 1 h at 700 rpm. Ready-to-print suspensions will be called inks. The compositions of the different inks studied here are given in Table 1.

Each ink is printed by using a piezoelectric ink-jet printer specifically designed for R&D and feasibility testing. It is recommended for this printer to design inks with a viscosity between 10 and 12 mPa s, a surface tension from 28 to 33 mN m, a boiling point under 100 °C and a particle size lower than 200 nm to limit nozzle clogging, among other things. Deposition is done onto an aluminum current collector warmed at 30 °C during the printing operation. Printing pattern is a 6 mm diameter disk. The distance between the nozzles and the aluminum current collector substrate was fixed at 800 μm. The nozzles of the printer eject the ink, with the following ejection parameters: 15 kHz as jetting frequency and 16 V of voltage on each nozzle (Fig. 1). Pulse waveform is also applied during non-jetting step to work against particles agglomeration in the ink.

Several printing lines (5, 20 or 40) per pattern are deposited, which determines the active mass loading on the pattern. Drying is done during 24 h at 60 °C and then 24 h at 100 °C under vacuum to remove water before battery assembly. Ink 3 was also deposited by tape casting for the sake of comparison. This tape-casted electrode has 0.5 $mg.cm^{-2}$ of active material loading, is 7 μm thick, which corresponds to 70% of porosity.

2.3. Battery assembly

$LiFePO_4$-based composite electrodes are assembled in electrochemical cells (Swagelok) with lithium metal and glass fiber separator soaked in an electrolyte. Two electrolytes are used: one consisting of a 1 M $LiPF_6$ solution in an ethylene carbonate-dimethyl carbonate (EC-DMC 1/1vol) mixture (from Novolyte), namely LP30, and one consisting of a 0.5 M lithium bis(trifluoromethane)sulfonylimide salt (Li-TFSI) in N-methyl-N-propylpyrrolidinium bis(trifluoromethane)suflonylimide ionic liquid (PYR13-TFSI) (from Solvionic), called here ES (Electrolytic Solution). The assembly of Swagelok cells is carried out in a dry glove box under argon atmosphere.

2.4. Characterization

2.4.1. Ink characterization

Rheological properties are measured on Anton Paar rheometer (Physica MCR 101) with a 50 mm diameter plane-and-plane geometry and analyzed with Rheoplus software. Before measurement starts, the sample is equilibrated at 20 °C. Pre-shearing of the sample (here at 1000 s^{-1} for 45 s) is necessary for a good reproducibility of the measurements. It ensures that all samples have the same mechanical history. Viscosity, or shear stress, is then measured as a function of the shear rate from 0.1 to 1000 s^{-1} and 1000 to 0.1 s^{-1} to determine the flow properties. Storage and loss moduli, G' and G'' respectively, are measured, on the one hand as a function of strain with constant frequency and on the other hand as a function of time with constant strain and frequency. These measurements are used to determine the flow properties and to probe the stability of the inks in the cartridge of the printing machine.

2.4.2. Electrodes characterization

Scanning electron microscopy (SEM) imaging is performed using a JEOL JSM 7600F to study the morphology of the electrodes. Electrochemical experiments are performed at 20 °C, monitored by a VMP biologic instrument, with potential limitation of 4.0 V in charge (upper cut-off potential) and 2.5 V in discharge (lower cut-off potential) versus Li^+/Li.