Journal of Power Sources 274 (2015) 1085–1090

Contents lists available at ScienceDirect

Journal of Power Sources

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

Toward fast and cost-effective ink-jet printing of solid electrolyte for lithium microbatteries

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HIGHLIGHTS

- Silica based ionogel are solid electrolyte as efficient as ionic liquid based electrolyte.
- Ink-jet printing of these ionogels' sol precursors is efficient.
- Consequently, ionogels are shown processable for microbatteries technology.
- This affords cost effective and fast deposition of safe and thermal resistant electrolytes.
- Tests with full Li-ion cell showed 100 cycles at 300 μAh cm^{-2}.

ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form
19 September 2014
Accepted 17 October 2014
Available online 29 October 2014

Keywords:
Ionogel
Ionic liquid
Ink-jet printing
Sol–gel silica
Lithium microbattery
Cycling

ABSTRACT

Ink-jet printing of ionogel for low-cost microbattery is presented. Such an approach allows to provide liquid-like electrolyte performances for all-solid microdevices. Ink-jet printing process is possible thanks to sol precursor of the ionogel. This full silica based ionogels confining ionic liquid are known to be thermal resistant, serving safety and technologies requiring solder reflow. High ionic conductivity and compatibility with porous composite electrodes allow reaching good electrochemical cycling performance: full Li-ion cell with $LiFePO_4$ and $Li_4Ti_5O_{12}$ porous composite electrodes shows a surface capacity of 300 μAh cm^{-2} for more than 100 cycles. Such surface capacities are very competitive as compared to those obtained for microdevices based on expensive PVD processes.

1. Introduction

Energy storage is a great challenge to answer the important and increasing needs of society. Lithium batteries are well known and used for lots of mobile applications (computer, cell phone, EV, …) because of their high energy density. Current research is mostly focused on improving all factors (higher voltage at the positive electrode, higher capacity, longer cycle life, cheaper active material …) that play on the cost and the energy density of the batteries in view of the development of electric vehicles and storage of renewable energies. On another hand and in another direction there is a big demand for microsources of energy, i.e. microbatteries [1,2]. Applications requiring microsources of energy can be active radio-frequency identification (RFID), autonomous sensors network, smart cards, implanted medical devices, etc.

First developments about microbatteries were reported by Kanehori [3]. Requirements for microbatteries are surfaces about mm^2 to cm^2 with less than mm thickness, all solid state design for microelectronic integration. Subsequently, these requirements are significantly different than that of standard Li-ion batteries which use liquid electrolytes impregnated in a separator membrane.

The solid electrolyte used in microbatteries has to be a good ionic conductor and a very poor electronic conductor in order to avoid self-discharge; it must present good thermal and electrochemical stabilities, as well as sufficient mechanical properties to physically separate positive and negative electrodes without short circuits. Finally the solid electrolyte requires a compatible deposition process on one of the two electrodes and shall be compatible with the other electrode deposition.

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http://dx.doi.org/10.1016/j.jpowsour.2014.10.164

At present, the standard way to fabricate microbatteries is Physical Vapor Deposition (PVD) of dense layers (electrodes and electrolyte). Typically LiPON is used as solid state electrolyte, [4,5] $LiCoO_2$ as positive electrode and lithium metal as negative electrode. The solid electrolyte can limit power performance due to its low ionic conductivity in comparison with standard liquid electrolyte. Moreover, low ionic diffusion in dense (non-porous) electrodes results in supplementary limitations when higher energy density is required, i.e. when electrodes thickness increases. One way to circumvent these limitations is the use of three dimensional (3D) architecture instead of planar architecture [6,7]. Nevertheless, such 3D design does not allow a constant distance between electrodes and it turns out to be difficult to obtain homogeneos current densities in the microbattery [8]. Still, the design of 3D microbatteries are very promising for improving energy density but they are not achieved up to now and they will be implemented at the price of higher cost.

Processes of deposition like spray, ink-jet or screen printing should allow cost reduction for the fabrication of microbatteries because the equipments are much cheaper than PVD machines and deposition rates are much faster [9].

Subsequently, our strategy is to develop low cost microbatteries with ink-jet printed solid electrolyte and porous composite electrode for microelectronic technology. Since ink-jet printing is compatible with sol–gel processes, we have merged our knowledge on microbatteries with that on confining ionic liquids (ILs) to obtain solid and safe electrolytes, named ionogels. Silica based chemical ionogels are good candidates for microbatteries because of their high ionic conductivity, shaping ability and thermal resistance which is required for sustaining the solder reflow process. The sol gel route used to synthesize ionogel [10] was already shown to be compatible with porous composite electrodes [11]. We show herein that ionogel printing can be used in order to develop a fast, solid electrolyte deposition process, resulting in microbattery with high level of performances. The electrodes used here are porous and around 10 μm thick, thus thicker than the typical 1–5 μm dense PVD electrodes.

2. Experimental

2.1. Materials

Ionogel is obtained by sol–gel route as presented previously [10,11]. The mesoporous silica host structure is obtained by polycondensation of tetramethyl orthosilicate (TMOS, Sigma Aldrich). The confined ionic liquid is here N-methyl-N-propylpyrrolidinium bis(trifluoromethan)suflonylimide (PYR13-TFSI), with an added Li salt lithium bis(trifluoromethan)sulfonylimide (Li-TFSI): the resulting PYR13-Li-TFSI is the electrolytic solution denoted further ES. The IL/TMOS, and IL/Si, molar ratio studied here are 0.25 and 1.

Homogenous porous composite electrodes are used as working electrodes. They contain an active material powder, a polymeric binder and an electronic conductor powder [12]. This type of electrode is here obtained by tape casting an aqueous slurry (the different powders dispersed in the polymer solution).

The positive and negative electrodes are based on carbon-coated lithiated iron phosphate ($LiFePO_4$) and lithium titanate ($Li_4Ti_5O_{12}$) at the positive and negative sides, respectively. $LiFePO_4$ has a carbon content of about 3 wt.%, and a specific surface area of 20 $m^2\ g^{-1}$. The size of the primary particles is in the [60–100 nm] range for $LiFePO_4$ and [40–100 nm] for $Li_4Ti_5O_{12}$. The binder used is the carboxyl methyl cellulose (CMC) from Sigma–Aldrich with 0.7 mol carboxyl per mol cellulose and a molar mass of 250,000. Carbon black chosen as electronic conductor additive is a Carbon Super P™ (C_{SP}) from Timcal with a specific surface area of 60 $m^2\ g^{-1}$, with primary spherical particles from 10 nm to 90 nm.

2.2. Electrode elaboration

Positive and negative electrodes are separately prepared with the same process, detailed for the positive electrode. For the preparation of the positive electrode slurry, $LiFePO_4$, CMC and C_{SP} are dispersed in deionized water with a total solid fraction of 20 wt %. Magnetic stirring for 12 h is used for pre-mixing the slurry. Then, ball-milling at 700 rpm during 1 h is used to pulverize the remaining agglomerates of powder and achieve a good homogeneity of the slurry. The latter is thereafter tape cast on aluminum current collector. The final step is a drying 24 h at room temperature followed by a 24 h at 100 °C under vacuum to remove residual water. Positive electrode thickness is 10 μm, with 0.8 mg cm^{-2} loading and 75% of porosity. Composition ratio of dried electrode is 80 wt% of active materials, 8 wt% of CMC and 12 wt% of C_{SP}. Slurry with $Li_4Ti_5O_{12}$, CMC and C_{SP} is similarly prepared and tape cast on aluminum current collector to obtain the negative electrode with similar parameters.

2.3. Ink-jet ionogel printing

The ionogel is obtained after ionogel precursor printing, using Dimatix DMP2800 ink-jet printer and subsequent sol–gel polycondensation. Each nozzle contains a piezoelectric working as a pump to eject the droplets. The 16 nozzles of the Dimatix cartridge eject the ionogel sol precursor. The gap between the nozzles and the porous composite electrode was fixed at 800 μm. Several layers deposition is required to obtain ionogel with enough thickness to act as a separator. Droplets are generated using ejection frequency of 15 kHz and voltage of 16 V on the 16 nozzles. Before all following steps, the water was carefully removed by drying under vacuum at 100 °C during 24 h.

2.4. Battery assembly

In a first step, half cells are prepared with tape cast positive electrode with ionogel solid electrolyte printed on the top.

The positive electrode/ionogel is assembled with lithium metal as counter electrode in a Swagelok electrochemical test cell to form a half cell. Fiberglass separator soaked in PYR13-TFSI and Li-TFSI solution is added between the counter Li metal electrode and the ionogel solid electrolyte to obtain good surface wetting contact between both solid layers. This first step is used to validate the assembly of the positive electrode with the ionogel solid electrolyte.

Then, $LiFePO_4$ positive and $Li_4Ti_5O_{12}$ negative porous composite electrodes, both coated by an ionogel solid electrolyte layer are inserted face to face in a Swagelok cell to build a Li-ion cell. A fiberglass separator soaked in PYR13-TFSI and Li-TFSI solution is nevertheless inserted to have a good wetting contact between the two solid electrolyte ionogel surfaces. Otherwise, a high polarization of the cell results from the contact between the two solid bodies ($LiFePO_4$ electrode/ionogel and $Li_4Ti_5O_{12}$ electrode/ionogel). The different steps for assembling both types of cells are described in Fig. 1. The assembly of Swagelok test cells is carried out in a dry glove box under argon atmosphere.

2.5. Characterizations

All electrochemical experiments are monitored by a VMP biologic potentiostat/galvanostat operated with EC-Lab software.