

## **Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiFePO<sub>4</sub> Solid-State Lithium-Ion Full Cell with Lithiated Nafion membrane**

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The present work studies the solid-state lithium-ion full cell Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiFePO<sub>4</sub> with propylene carbonate swollen lithiated Nafion membrane (Li-Nafion) as both electrolyte and separator, and lithiated Nafion dispersion – as a binder. The advantage of this cell is single-ion lithium conductivity of the polymer electrolyte preventing its polarisation, as well as the absence of a liquid phase and negligible vapour pressure of the high-boiling-point plasticiser increasing the safety of the device. The galvanostatic charge/discharge tests examined the electrochemical performance of the full cell, as well as Li/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and Li/LiFePO<sub>4</sub> half-cells. With a commonly used mass ratio of composite electrodes (active material/carbon black/binder of 80:10:10), the discharge capacity of the full cell Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Li-Nafion/LiFePO<sub>4</sub> as studied for the first time was about 70 mAh g<sup>-1</sup> at 50th charge-discharge cycle at coulombic efficiency of 99%. A more proper plasticiser and optimisation of the mass ratio of the components of the electrodes can render such a cell suitable for application in LIBs with enhanced safety.

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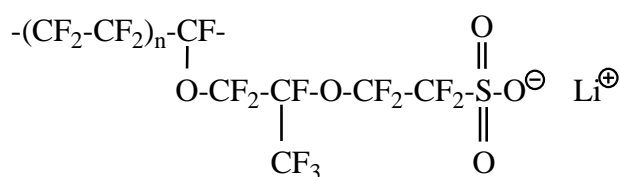
**Keywords:** Lithium-ion battery; Electrochemical performance; Lithiated Nafion; Lithium iron phosphate; Lithium titanate

### **1. INTRODUCTION**

As presently the most efficient energy storage devices for portable electronics and power tools, lithium-ion batteries (LIBs) play a significant role in daily life. Additionally, LIBs are a promising means for providing power for emerging applications including hybrid electric vehicles, pure electric vehicles and energy storage systems [1, 2]. New areas of their usage make safety a top priority in the design of the electrochemical system. Non-flammable polymer electrolytes seem to be most suitable when

replacing the liquid electrolyte in the aims of improving the safety performance of LIBs. Furthermore, the polymer electrolyte can play three crucial roles in a battery: it is a lithium-ion carrier; it acts as an electrode spacer (separator); and it is a binder for composite electrodes [3]. In addition, these materials can be used in thin, flexible solid-state batteries manufactured in different geometrical configurations and free from electrolyte leakage [4-8].

A promising approach to the development of polymeric lithium-ion batteries may be to use lithiated perfluorinated sulphonic ion-exchange membranes swollen with low-molecular-weight aprotic solvent. Here, the required high mechanical, chemical and thermal stability of the membranes is supported by the perfluorinated backbone [4]. As a consequence of their high proton conductivity in aqueous media, commercially-available perfluorinated ion-exchange membranes Nafion manufactured by Dupont are used extensively in proton-exchange membrane fuel cells (PEMFC), sensors, vanadium redox flow batteries (VRBs) and electro organic syntheses [4, 9-15]. As is known, Nafion can be easily converted from the H<sup>+</sup> form into different cationic forms (including Li<sup>+</sup> type) [11] while maintaining excellent stability. Since sulphonic anions are chemically bonded to the side chains of the polymer (Fig. 1), the only mobile species in lithiated Nafion (Li-Nafion) are Li<sup>+</sup> ions, with the result that the transference number achieves unity [3, 4]. For application in LIBs, such polyelectrolyte has apparent advantages over conventional polymer electrolytes in which both cation and anion are free to move. Consequences of polarisation occurring due to bipolar conductivity include voltage loss, higher internal impedance and undesirable side reactions, as well as, eventually, cell failure [7]. In contrast, single-ion lithium conductivity prevents concentration polarisation and provides for much better cell performance, even if the conductivity of the polyelectrolyte is as much as order of magnitude lower than that of a conventional polymer electrolyte [16-18]. Therefore, the Li-Nafion membrane swollen with aprotic solvent, even with moderate conductivity [19-26], seems to be a suitable choice for the development of a polymeric lithium-ion battery.



**Figure 1.** Structural formula of Li-Nafion

Li-Nafion membranes swollen with aprotic solvents have been successfully tested as a functional separator for Li-S cells (see, for example, Refs. [14, 27-29]). An improvement in cycle performance and coulombic efficiency relative to the liquid electrolyte Li-S cell was observed in such cells due to the suppression of polysulfide anions diffusion through the ionomer film. This helped to reduce the loss of sulphur active mass and the corrosion of Li electrode, and inhibit the undesirable “shuttle phenomenon”. Surprisingly, other lithium electrochemical systems with Li-Nafion attract much less attention. Liang et al. [13] studied the electrochemical performance of Li/LiCoO<sub>2</sub> cells with Li-Nafion, swollen with propylene carbonate (PC)/ethylene carbonate (EC) mixture, and Cai et al. [4] described Li/LiFePO<sub>4</sub> cells

with a Nafion-type lithiated perfluorinated sulphonic ion-exchange membrane swollen with PC. The results demonstrated that the ionomer electrolyte is usable in rechargeable Li-metal batteries and the cathode half-cells of LIBs. However, as it was emphasised in Ref. [30], the excellent performance achieved with half-cells is not necessarily reproducible into high-performance full cells. In contrast to full cells with a definite amount of Li, half-cells contain a theoretically infinite source of Li. Therefore, half-cells are suitable for studies of the mechanisms of electrochemical processes with an active material but can hardly be used to forecast the behaviour of full-cells [30]. As far as we know, there is no published research on the performance of anode half-cells of a lithium-ion battery or their full cells using Li-Nafion as electrolyte/separator and binder.

This paper reports our preliminary results on the full cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)/ $\text{LiFePO}_4$  (LFP) and the separately studied anode and cathode half-cells with Li-Nafion binder and Li-Nafion membrane swollen with PC as a solid-state electrolyte. A safe and fast-charging LTO/LFP electrochemical system is applied in commercial LIBs with liquid or gel electrolytes. The Li-Nafion membranes may be promising for application in such solid-state lithium-ion batteries with enhanced safety and in the flexible thin-film LIBs.

## 2. EXPERIMENTAL

### 2.1. Materials

Pre-treatment, neutralisation by LiOH, drying and swelling in PC of a commercial Nafion®-115 membrane (Du Pont, 125  $\mu\text{m}$  thickness) were performed as described in [21]. Nafion® Dispersion (Ion Power Inc., USA) was neutralised to  $\text{Li}^+$  form by adding 1 M aqueous LiOH solution until  $\text{pH}=7$ . The weight content of the polymer in the resulted Li-Nafion dispersion used as a binder in composite electrodes was 10%.

$\text{LiFePO}_4$  was purchased from GelonLIB (China).

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  was prepared by solution combustion synthesis. The phase composition of the product was controlled by X-ray diffraction (Shimadzu XRD-7000 diffractometer,  $\text{Cu K}\alpha_1$  radiation,  $2\theta=10\text{-}80^\circ$ ) using the ICDD-ICPDS database.

Liquid electrolyte 1M  $\text{LiPF}_6$  in EC/EMC (1:1, v/v) was prepared from components supplied by Sigma Aldrich and used without further purification.

### 2.2. Electrodes preparing

The composite electrodes were prepared by inkjet printing a homogenised mixture of the active material (LFP or LTO), a conductive additive (acetylene black Super P provided by Gelon LIB (China)) and Li-Nafion dispersion as a binder onto an aluminium (positive electrode) or copper (negative one) foil. The weight ratios of the dry components were 80:10:10, respectively, for both positive and negative electrodes. The electrodes thus obtained were dried under vacuum at 120  $^\circ\text{C}$  for 12 h, compacted in a rolling press and then impregnated into PC for 1 h. The loading of the active material was about  $5 \text{ mg}\cdot\text{cm}^{-2}$  for both positive and negative electrodes.

### 2.3. Electrochemical measurements

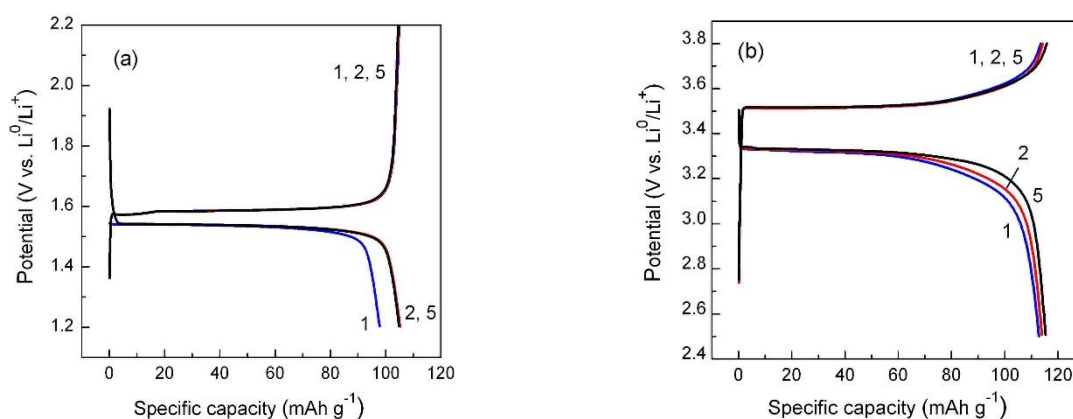
The electrochemical behaviour of the half/full cells with PC swollen Li-Nafion as electrolyte/separator and binder was tested with two-electrode pouch cells assembled in an Ar-filled glove box with O<sub>2</sub> and H<sub>2</sub>O contents < 0.1 ppm. The half-cells contained composite electrode (LFP or LTO) and lithium-foil counter electrode (Li foil (99.9%), Alfa Aesar (USA)) with an active surface of 2.25 cm<sup>2</sup> separated by the PC swollen Li-Nafion film with the larger area. The full cell LTO/LFP PC with PC swollen Li-Nafion membrane possessed the same geometry. Full cell with the same electrodes and baseline liquid electrolyte 1M LiPF<sub>6</sub> in EC/EMC (1:1, v/v) was also assembled; Celgard 2300 film served as a separator.

Cycling performance and rate capability of the cathode and anode half-cells were examined at 25°C by galvanostatic charge-discharge curves measured with P-20X80 multichannel potentiostat (“Elins” LLC, Russia) in the voltage ranges of 2.5–3.8 and 1.2–2.2 V vs. Li<sup>0</sup>/Li<sup>+</sup>, respectively. Current density varied from 0.05 to 1C (1C= 170 mA g<sup>-1</sup>). For the full cell, the voltage range was 1.0–2.6 V vs Li<sup>0</sup>/Li<sup>+</sup>. The calculations of specific capacity were based on the mass of the active material (LTO or LFP) in the electrode mixture for the half-cells and the mass balance of LTO and LFP for the full cell.

## 3. RESULTS AND DISCUSSION

### 3.1. Galvanostatic cycling: half-cells

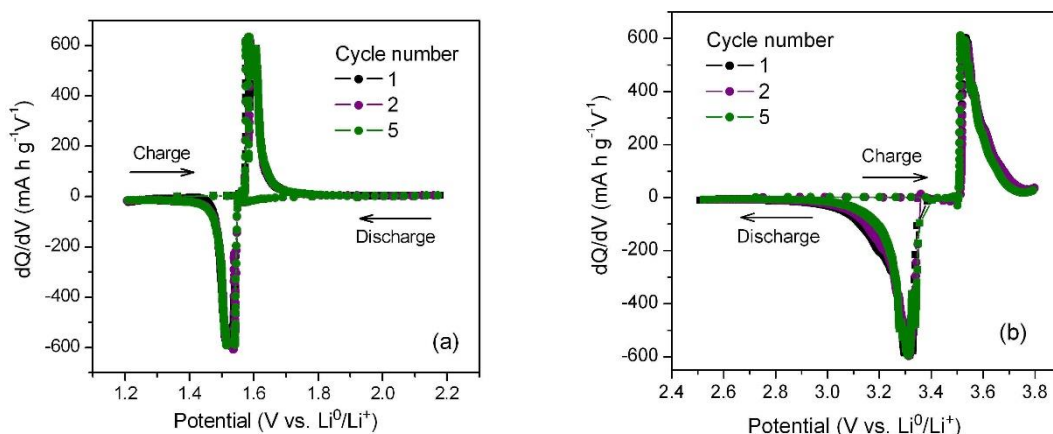
The electrochemical performance of the LiFePO<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> materials in solid-state cells with PC swollen Li-Nafion as electrolyte/separator and binder in the composite electrodes were first tested separately in half-cells with Li metal. (It should be recalled that cathode half-cell Li/LFP is of independent interest as a prototype for rechargeable solid-state Li-metal battery with polymer electrolyte).



**Figure 2.** Charge-discharge curves of the 1<sup>st</sup>, 2<sup>nd</sup> and 5<sup>th</sup> cycles for the anode Li/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (a) and cathode Li/LiFePO<sub>4</sub> (b) half-cells with PC swollen Li-Nafion as electrolyte/separator and binder at 0.05C charge/discharge rate

Fig. 2 presents plots of galvanostatic charge/discharge curves at the first five cycles for cathode and anode half-cells measured at 25 °C at a low rate of 0.05C. The voltage ranges were 2.5–3.8 V for LFP and 1.2–2.2 V for LTO (*vs*  $\text{Li}^0/\text{Li}^+$ ) (following Refs. [31–34]). The difference between the median voltages of charge and discharge of the Li/LTO cell was ~ 50 mV at any cycle smaller than that of the Li/LFP cell (~185 mV) (Fig. 2). The observation indicates that the Li/LTO cell has lower internal resistance than Li/LFP one.

For the anode half-cell Li/LTO, the charge and discharge capacities of the first cycle were 98 and 105 mAh  $\text{g}^{-1}$  respectively. The coulombic efficiency of the second cycle was about 98%, and this value did not change upon the following cycling, as well as charge/discharge curves (Fig. 2(a)). For the cathode half-cell Li/LFP, both charge and discharge curves showed practically no change upon cycling after the first five cycles. It can be seen that the discharge capacities slightly increased during these cycles (Fig. 2(b)). The charge and discharge capacities of the first cycle of the cathode half-cell were 114 and 113 mAh  $\text{g}^{-1}$ , respectively, resulting in a coulombic efficiency of about 99%. The high coulombic efficiency values indicate that the processes of lithium insertion/extraction into both electrode materials are highly reversible and proceed without the contribution of side reactions. The plateaus at ~3.3 and ~1.55 V are typically attributed to the topotactic insertion/extraction of lithium by two-phase mechanism in the  $\text{LiFePO}_4\text{-FePO}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-Li}_7\text{Ti}_5\text{O}_{12}$  systems respectively [32, 33, 35].

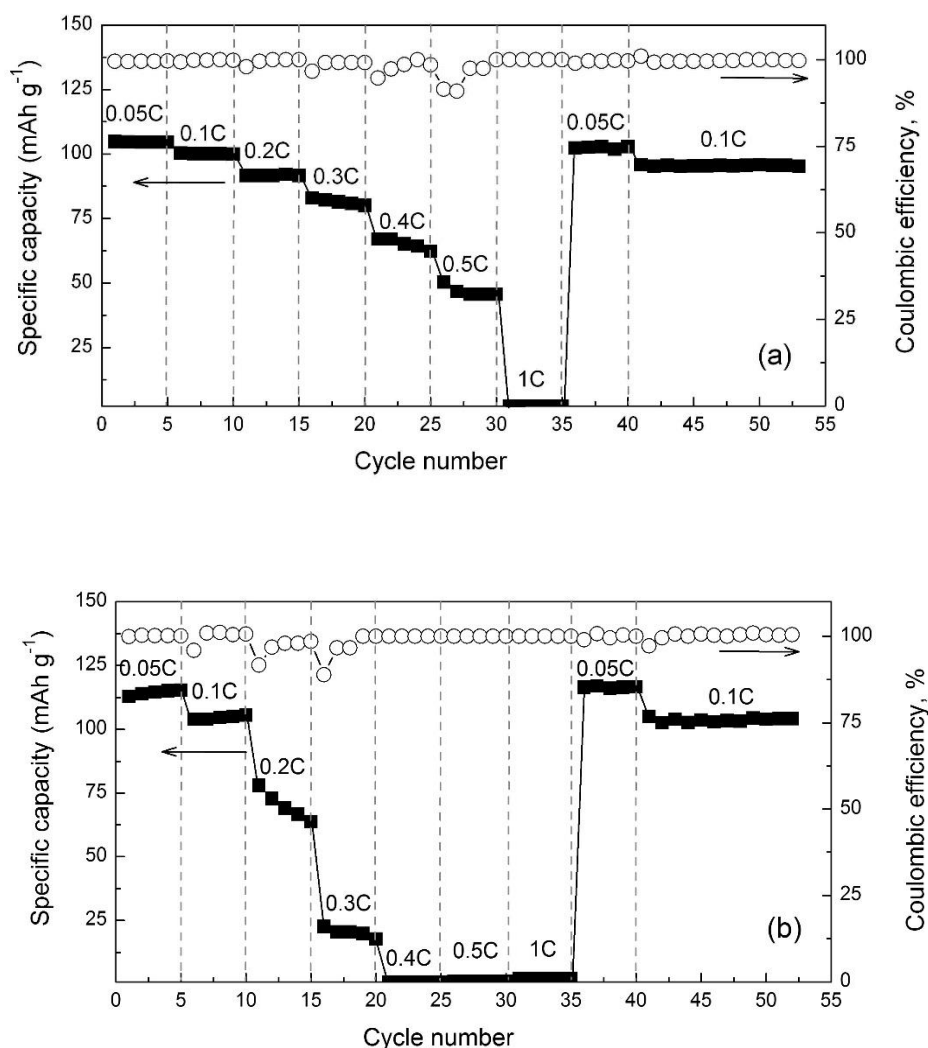


**Figure 3.** Different capacity vs. voltage curves of the 1<sup>st</sup>, 2<sup>nd</sup> and 5<sup>th</sup> cycles for the Li/LTO (a) and Li/LFP (b) cells with PC swollen Li-Nafion as electrolyte/separator and binder at 0.05C charge/discharge rate

The plots of the differential capacity ( $dQ/dV$ ) vs. voltage at the 1<sup>st</sup>, 2<sup>nd</sup> and 5<sup>th</sup> cycles shown in Fig. 3 clarify the details of the charge/discharge curves of anode Li/LTO (a) and cathode Li/LFP (b) half-cells. As can be seen the Li/LTO cell (Fig. 3(a)) exhibited a pair of flattened peaks, the oxidation peak centred at about 1.59 V and the reduction peak centred at 1.53 V. This may be explained in terms of the two-phase oxidation / reduction reactions of the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  couple in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , compensated by extraction–insertion of lithium [34]. The small difference in the potentials of the cathodic and anodic peaks  $\Delta E \sim 0.06$  V possibly indicates insignificant polarisation of the LTO electrode [34] and quite good

reversibility of  $\text{Li}^+$  insertion/extraction into the lithium titanate structure. Unlike the anode half-cell, the Li/LFP cell exhibits complicated anodic and cathodic peaks centred at 3.31 and 3.53 V, respectively (Fig. 3(b)). These both display quite sharp maxima that correspond well to the two-phase charge/discharge reaction of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple. The distinct shoulder observed at the reduction peak near 3.21 V during 1<sup>st</sup> and 2<sup>nd</sup> cycles disappeared at 5<sup>th</sup> and following ones. Significant differences in the potentials of the cathodic and anodic peaks  $\Delta E \sim 0.22$  V reflects the much higher polarisation degree of the LFP electrode as compared with LTO one.

### 3.2. Galvanostatic cycling: various charge-discharging rates



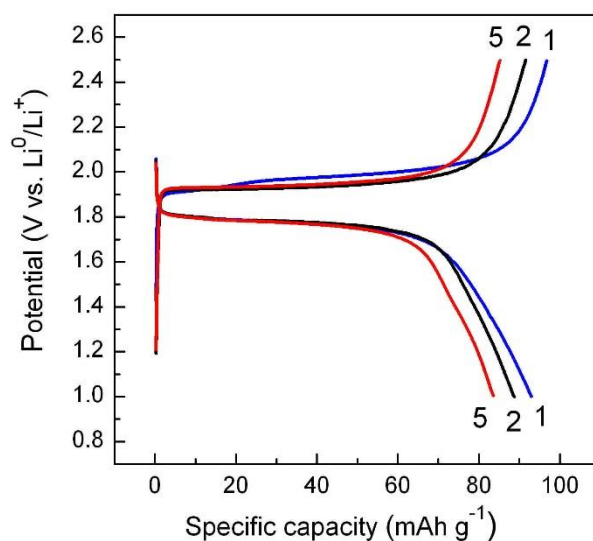
**Figure 4.** Cyclic performance of the Li/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (a) and Li/LiFePO<sub>4</sub> (b) half-cells with PC swollen Li-Nafion as electrolyte/separator and binder at different charge-discharge rates

To further evaluate the electrochemical performance of the half-cells with PC-swollen Li-Nafion as electrolyte/separator and binder, the Li/LTO (a) and Li/LFP (b) cells were tested under various charge-discharging rates. Fig. 4 demonstrates the results of these measurements. It can be seen that the rate capability of both anode and cathode half-cell is poor: the discharge capacity decreases rapidly with the increasing rate. The rate capability of the Li/LTO cell herein is noticeably better than those of the Li/LFP cell: discharge capacity tends to zero at 1C for LTO and 0.4C for LFP. It is worth noting, however, that the initial values of the discharge capacity of both cells were restored when the rate decreased again to the minimal value of 0.05C (Fig. 3).

The fact that the cells did not lose their initial capacity can be ascribed to kinetic limitations rather than the degradation of active materials LTO and LFP. At high rates, charge-discharge processes are known to be governed by the diffusion of lithium ions through the electrolyte and the electrode/electrolyte interface [34].

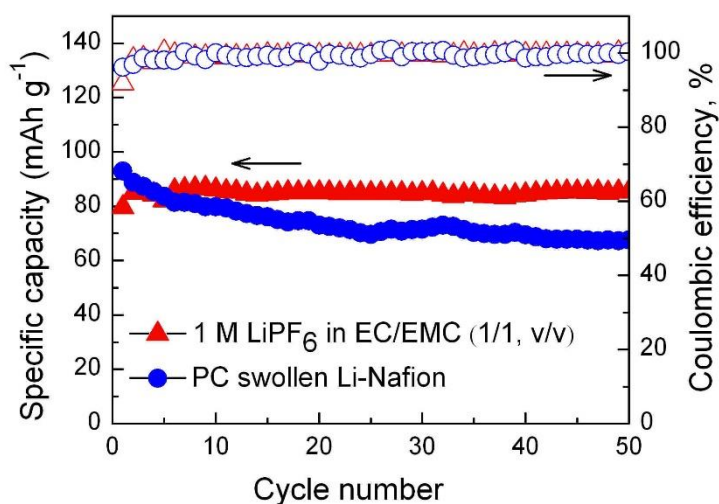
### 3.3. Galvanostatic cycling: full-cell

Since the rate capability of both anode and cathode half-cells was poor, the rate of 0.1 C was used to test the cycling performance of the full cell. Fig. 5 shows charge-discharge curves for the LTO/LFP cell. A voltage plateau at ~1.8 V is clearly seen at discharge curves. The discharge capacity of the first cycle was 93 mAh g<sup>-1</sup>. It smoothly decreased to 70 mAh g<sup>-1</sup> during 25 cycles, and was further almost unchanged up to 50th cycle with a coulombic efficiency of 99 %. Thus, the specific capacity of the full cell showed quite modest, albeit quite stable values upon cycling.



**Figure 5.** Charge-discharge curves for the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$  full cell with PC swollen Li-Nafion as electrolyte/separator and binder (charge/discharge rate was 0.1C)

The obtained results support the conclusion that the inadequate discharge capacity of LTO/LFP test cells was caused by the improper organisation of composite electrodes (most of all, positive one) rather than a degradation of the active materials or polymer electrolyte film. Here, it should be clarified that the commonly-used ratio of active material, carbon black and binder of 80:10:10 (by mass) were applied in composite electrodes with LTO and LFP without optimisation. Moreover, the conductivity of PC swollen Li-Nafion membrane is quite low ( $\sim 10^{-5}$  at room temperature [21]). Finally, the thickness of the PC swollen Li-Nafion film was too large (166  $\mu\text{m}$  compared with 20-25  $\mu\text{m}$  for the separator in commercially available LIBs). As shown in Ref. [29] for Li-S cells, the quantities of Li-Nafion binder and acetylene black in the composite electrode need to be optimised in order to achieve a balance between ionic and electronic conductivities [29]. Such a balance allows for the enhancement of specific capacity, improvement of rate capability and cycling performance of solid-state cells with Li-Nafion membrane. Moreover, a suitable choice of solvents for Li-Nafion swelling supports a significant increase in electrolyte conductivity as follows from Refs. [21-26]. Fig. 6 confirms this view. It is easy to see that the substitution of Li-Nafion with highly conductive liquid electrolyte gives a stable cycling and noticeable increase in specific capacity of the full cell (up to 85  $\text{mAh g}^{-1}$ ). Non-optimal electrode composition and low conductivity of polymer electrolyte also explain the comparatively low values of the specific capacities of both active materials (see Fig. 3). Thus, further work is needed to optimise the mass ratio of the components of positive and negative electrodes with Li-Nafion binder and to find more effective solvent for Li-Nafion swelling.



**Figure 6.** Cyclic performance of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$  full cell with PC swollen Li-Nafion membrane compared to the full cell with the same electrodes and baseline liquid electrolyte 1M  $\text{LiPF}_6$  in EC/EMC (1:1, v/v)



#### 4. CONCLUSION

The lithiated form of the Nafion membrane, swollen with propylene carbonate, can be regarded as a promising solid-state electrolyte/separator and binder in a battery with a negative electrode based on  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and a positive electrode based on  $\text{LiFePO}_4$ . The advantage of such a cell is the absence of a liquid phase and negligible vapour pressure of the high-boiling-point plasticiser, which increases the safety of the device. The combination of thin electrodes obtained by inkjet printing with a solid polymer electrolyte makes it possible to achieve flexible thin-film batteries. The discharge capacity of the full cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$  was  $68 \text{ mAh g}^{-1}$  at 50th charge-discharge cycle with a coulomb efficiency of 99%. The optimisation of the electrode mass composition and selection of a more effective plasticiser for Li-Nafion can significantly increase the discharge characteristics. This will be the subject of our further research. The Li-Nafion membranes swollen with aprotic solvent (or a mixture of solvents) may be promising for application in LIBs in the near future.

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