

Short communication

## LiFePO<sub>4</sub> water-soluble binder electrode for Li-ion batteries<sup>☆</sup>

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### Abstract

A new water-soluble elastomer from ZEON Corp. was evaluated as binder with LiFePO<sub>4</sub> cathode material in Li-ion batteries. The mechanical characteristic of this cathode was compared to that with PVdF-based cathode binder. The elastomer-based cathode shows high flexibility with good adhesion. The electrochemical performance was also evaluated and compared to PVdF-based cathodes at 25 and at 60 °C. A lower irreversible capacity loss was obtained with the elastomer-based cathode, however, aging at 60 °C shows a comparable cycle life to that observed with PVdF-based cathodes. The LiFePO<sub>4</sub>-WSB at high rate shows a good performance with 120 mAh g<sup>-1</sup> at 10C rate at 60 °C.

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### 1. Introduction

The successful commercialization of Li-ion gel polymer batteries for portable electronic devices has led to other applications where the thickness and weight of batteries are important. With regard to large size applications such as in EVs and HEVs [1,2], in contrast, lower-cost cathode materials are required. Recently, LiFePO<sub>4</sub> was investigated intensively as a potential cathode material for rechargeable Li-ion batteries [2–6] because of its low cost and safety. To improve the safety of the battery, more efforts must be focused on the type of binder used in the electrodes.

The poly(vinylidene fluoride) (PVdF) product has been most widely adopted as a binder for electrodes in Li-ion batteries. In the cell manufacturing processes, *N*-methyl-2-pyrrolidone (NMP) is generally used as a solvent to dissolve PVdF binder. Despite the widespread use of NMP, it has some disadvantages such as high cost, environmental issue associated with NMP recovery and the severe processing control of the relative humidity (to be less than 2%). The PVdF has strong binding strength, but low flexibility. The low flexibility of PVdF can easily dete-

riorate cycle life characteristics of the battery due to breaking of the bond between active materials when the active material and a carbon material and consequently expansion/contraction process occurs during charging and discharging. Therefore, in order to absorb the expansion and contraction stresses of the active material during charging and discharging, it has been suggested to adopt a binder having elasticity.

A new trend is now being developed to substitute the PVdF binder in the anode [7,8]. Many reasons have been brought up; safety aspect of the battery, its high cost and interest in high capacity. Fluorine is one of the degradation products in the battery that produces stable LiF. Depending on the liquid electrolyte, the formation reaction of LiF and other harmful products with double bond (C=CF-) is accelerated [9–11]. Furthermore, self-heating thermal runaway can be induced. With respect to safety, a binder such as PVdF, which is soluble in organic solvent, is dangerous to humans and the environment. Because the organic solvent used in electrode fabrication with PVdF must be recovered, alternative binders that are less costly and more environment friendly are essential. Consequently, our effort was focused on research to identify suitable alternative non-fluorinated binders. Some of the binders that were suggested include polyimide [13] and silica-based gel [12], unfortunately, most of these binders are soluble in organic solvent. Thus, the switch from non-aqueous to aqueous systems was imperative. Recently, aqueous binders have gradually replaced PVdF binders [8,13] for the anode material. The advantages of aqueous

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binders are as follows: (1) low cost, (2) no pollution problem, (3) enhancement of the active material ratio in a cell owing to the reduction of binder content, (4) no requirement for strict control of the processing humidity and (5) fast drying speed in electrode fabrication. SBR/CMC composite agent is generally used in the aqueous binder; styrene-butadiene rubber (SBR) is the primary binder and sodium carboxymethyl cellulose (CMC) is the thickening/setting agent. The aqueous binder has been widely applied in the anodes for Li-ion cells.

At present, effort has been started in the preparation of cathode slurry [14], however, the transition from the non-aqueous to aqueous coating process appears to have encountered some unexpected difficulties related to slurry formulation, viscosity control and film processing, which must be overcome for successful implementation in Li-ion batteries.

The binder material is one of the crucial electrode components for improved cell performance, for example, cycle life. In this regard, the elastomer is an attractive binder because it permits a high active material ratio and flexibility to the cathode compared to conventional PVdF binder. In addition, the water dispersion process of the slurry is environment friendly.

In this work, we report on the characterization of  $\text{LiFePO}_4$  cathode material that is obtained using a new water-soluble elastomer binder (WSB). The test results obtained with Li/gel electrolyte/ $\text{LiFePO}_4$  cells with  $\text{LiPF}_6$  salt in EC-DMC as the electrolyte are presented. These results are compared to those obtained with cathode using PVdF binder.

## 2. Experimental

$\text{LiFePO}_4$ -coated carbon powder was obtained from Phostech, Canada. The water-soluble binder is an elastomer obtained from ZEON Corp., Japan. This binder is an elastomer based on saturated organic compounds. The thickener is CMC (Daicel 2200, Daicel Chemical Industries Ltd., Japan). A slurry consisting of 90 wt.% of  $\text{LiFePO}_4$ , 6 wt.% carbon black, 2 wt.% CMC and 2 wt.% WSB by using water solvent was prepared by ball-milling. Mixing the slurry is very important to get a better dispersion of powders material in the polymer matrix and more uniform electrodes. In slurry preparation, more specifically, aqueous solution needs to have appropriate viscosity, uniform dispersion and no aggregation. The well-dispersed slurry between conducting carbon and CMC provides very uniform dispersion and uniform contact with  $\text{LiFePO}_4$  particles. The polymer (binder and CMC) ratio was adjusted to improve the adhesion of the particles to the current collector.

The coated film on aluminium collector was obtained by doctor blade method. For comparison, a PVdF-based electrode with 82 wt.%  $\text{LiFePO}_4$ , 6 wt.% carbon black and 12 wt.% PVdF is used. Before using the electrodes, they are dried for 24 h at  $120^\circ\text{C}$  under vacuum and cut in small surfaces with an area of  $2\text{ cm}^2$ . Coin-type Li/ $\text{LiFePO}_4$  cells with composite cathodes based on WSB and PVdF were evaluated. These cells contained gel polymer electrolyte with  $\text{LiPF}_6$  salt in EC/DMC (1:1). Charge–discharge cycling of the cells was carried out using the galvanostatic method (MacPile<sup>®</sup>, Claix, France). AC impedance spectroscopy was used to investigate interface phenomena. The

oxidation stability of the WSB was evaluated at 6.0 V. The cells were maintained at an optimum compression of 10 psi during cycling, at different rates between the voltage limits of 2.5 and 4 V.

## 3. Results and discussion

### 3.1. Physical properties

Some elastomers are commercially used as a binder for anodes in Li-ion batteries, however, for the cathode, successful implementation still remains a big challenge. The elastomers provide good flexibility to the anode even when used in very small amounts, which is beneficial for increasing the energy density of the battery. The compatibility of the elastomer binder compared to PVdF binder, and how they connect or interact with the  $\text{LiFePO}_4$  particles is different. Fig. 1 illustrates the binding models with elastomer and PVdF binders. Regarding the CMC, it is very hard to observe directly in the electrode structure. We speculate very thin CMC layer is coated at the active material of  $\text{LiFePO}_4$ , and some part acts as a rigid binder. During the aqueous slurry preparation process, the CMC is very important as a thickener to control the viscosity, but after coating the CMC stays almost unchanged in the electrode. CMC is an electrochemically inert part in the electrode and then eventually, has no significant role in the dried electrode. We consider that the elastomer contacts quite a small surface area of each particle. This contact is enough to ensure good binding and still gives flexibility to the electrodes. Thus, the binder absorbs the expansion and the contraction of the active material during the repeated charge and discharge since its flexibility is increased, so a battery having improved cycle life characteristics can be fabricated. In contrast, PVdF contacts a larger surface area that affects the electrode flexibility and battery cycling life.

The SEM photos in Fig. 2 show very uniform electrodes of  $\text{LiFePO}_4$  based on elastomer (a) compared to electrode with PVdF binder (b). The roughness of WSB-coated surface films is very low compared to that observed with PVdF films. This surface characteristic is a critical step before cell assembly. The PVdF cathode thickness varies from 28 to  $47.7\ \mu\text{m}$ , with a mean value of  $37.7\ \mu\text{m}$ . However, for the WSB cathode, the thickness varies from 42.5 to  $50\ \mu\text{m}$  with mean value of  $46.1\ \mu\text{m}$ . The electrode density was calculated for both binders. With the PVdF

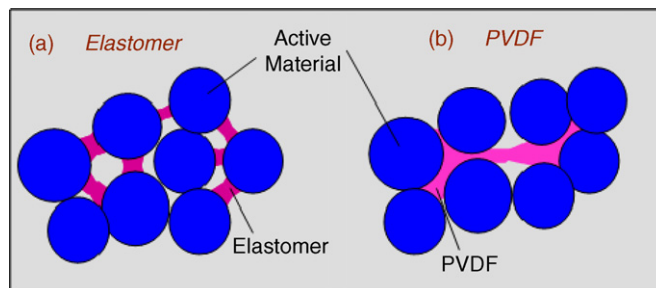


Fig. 1. Schematic images on binding structure between: (a) elastomer and (b) PVdF.

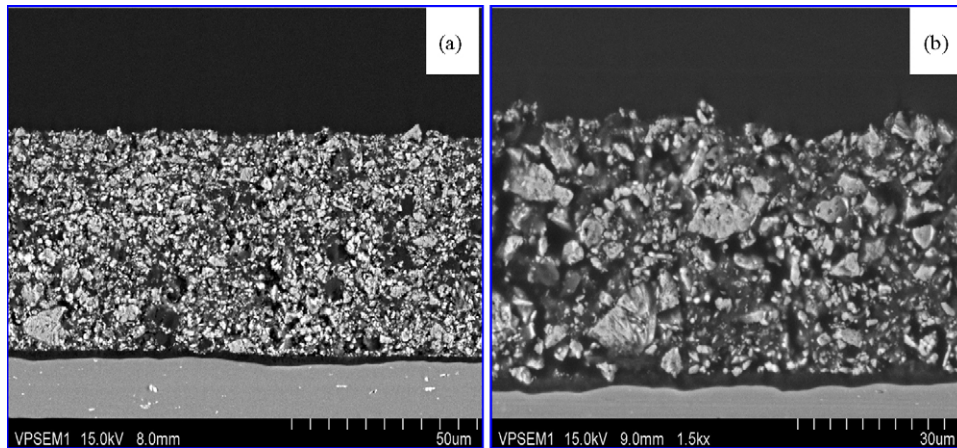


Fig. 2. SEM images of LiFePO<sub>4</sub> cathode material prepared by using elastomer (a) and PVdF (b).

cathode, the electrode density was 1.5 compared to 1.7 g cm<sup>-3</sup> for the WSB cathode. This result confirms the high flexibility of particles compaction during the coating process with WSB.

In order to evaluate the electrode flexibility, we developed the experimental apparatus shown in Fig. 3a. Thick films of the coated electrode (about 100 μm) were coated on an aluminium current collector. This electrode was cut into a 25 mm diameter circular shape and placed between two metal plates. Pressure was applied from above where the strain gauge is fixed. The pressure rate defined by the piston motion downward was adjusted at 0.35 mm s<sup>-1</sup> in order to have constant mechanical perturbation on the electrode. The pressure is applied continuously on the circular electrode until cracks appear. At this pressure level, we define the “crack point”. Then, the distance between the metal plates is recorded. As the pressure is increased the circular electrode is deformed. When the crack point appears, the height of the electrode ( $x$  in Fig. 3a) is measured. This measurement provides the degree of flexibility of the electrode (see Fig. 3b). Comparing the flexibility of elastomer binder and PVdF binder, it is apparent that the ZEON elastomer system is much more flexible (by a factor of 2) than the PVdF systems. The crack point increased when the amount of binder is reduced in both cases.

### 3.2. Electrochemical stability

An electrochemical cell consisting of glassy carbon (working electrode) and lithium metal (counter electrode) was used to determine the oxidation stability of the water-soluble binder and PVdF binder. The glassy carbon coated with a thin layer of the binder, WSB or PVdF, was scanned to anodic potentials. The limiting oxidation stability of the binders is presented in Fig. 4. The data show good oxidation stability of WSB, which did not show any current peaks up to 6 V. On the other hand, PVdF showed evidence for two degradation products by the two potential plateaus at 5.4 and at 6.5 V. These results suggest that the limiting oxidation potential increased by more than 0.6 V when WSB is used. Therefore, high voltage cathodes can be used with WSB without any polymer degradation up to 5 V. Upon oxidation, PVdF forms a degraded fluorinated polymer, and then eventually to HF. However, when WSB is used, the main polymer degradation product is based on the aromatic hydrocarbon structure.

We have used molecular orbital theory to calculate the orbital energy of the binders. The Hartree-Fock (HCTH/6-31G) method was applied in the mathematical calculation. The orbital energy was calculated for PVdF and ZEON elastomer binder

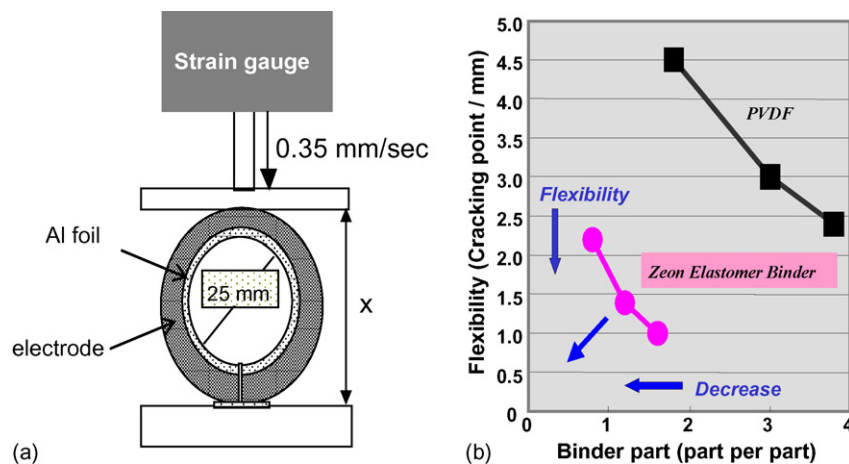


Fig. 3. Loop stiffness tester and (a) index for flexibility of electrodes by binder content (b).

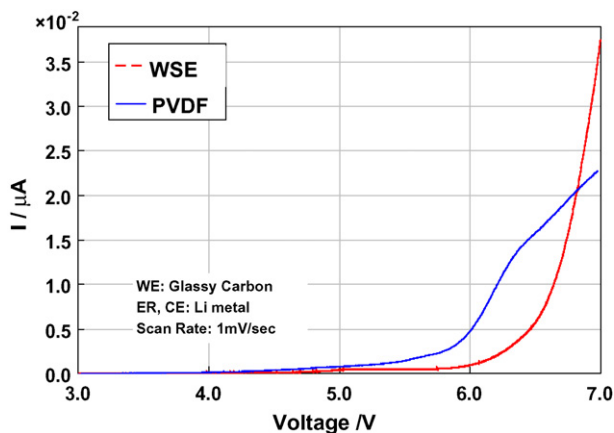


Fig. 4. Oxidation stability of WSB elastomer compared to PVdF.

compared to two electrolyte solvents ethylene carbonate (EC) and diethyl carbonate (DEC). The lower unoccupied molecular orbital (LUMO) and the higher molecular orbital (HOMO) are calculated by using Gaussian03 software. The values are obtained at vacuum standard. Comparing the HOMO data in Fig. 5, the elastomer shows the smallest value followed by PVdF, EC and DEC. This result indicates the relative tolerance of the elastomer binder and other materials (PVdF, EC and DEC) to electrochemical oxidation. From our analysis, we believe that the elastomer water-soluble binder can be used with a wide range of cathode materials.

### 3.3. Electrochemical performance

AC impedance measurements were performed with cells containing the elastomer cathodes and lithium metal counter electrode. Fig. 6 shows the impedance spectra of cells with cathodes that were pressed or not pressed. The data show only a small difference in the ohmic resistance before and after pressing; a slight decrease in the interface impedance from 10 to  $8 \Omega \text{ cm}^{-2}$  was observed after pressing. In addition, this data show very little effect of the lamination process on cathode side. The WSB has good inter-particle binding and good adhesion with the current collector.

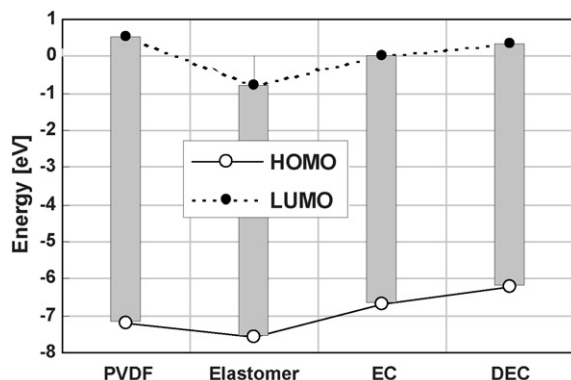


Fig. 5. HOMO/LUMO orbital energy for binder polymers and electrolyte solvents.

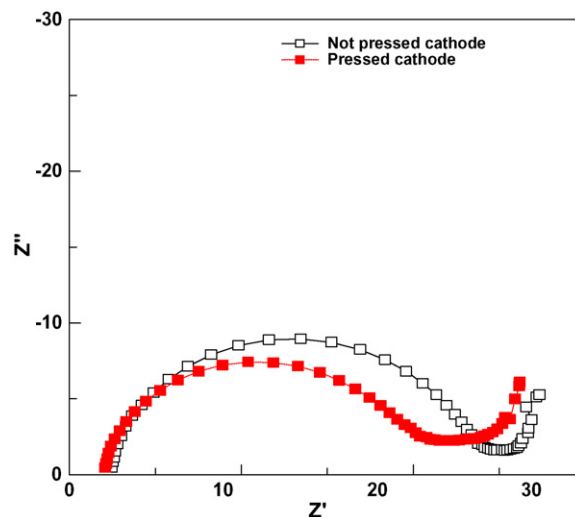


Fig. 6. Impedance measurement in Li/LiFePO<sub>4</sub> cells with and without cathode pressing.

Fig. 7 shows the first cycle at 25 °C of cells having LiFePO<sub>4</sub> cathodes with PVdF and WSB binder. The first coulombic efficiency shows a comparable value with 92.7% for PVdF and 92.6% elastomer binder. However, higher reversible capacity was obtained with elastomer binder. The reversible capacity was 148 and 157 mAh g<sup>-1</sup>, respectively, with cathodes containing PVdF and WSB. This difference is mainly due to the optimum contact inter-particles of both LiFePO<sub>4</sub> and conductive carbon materials.

The first electrochemical performance was characterized with low rate charge–discharge cycling at C/24 rate. The curves in Fig. 8 show the first cycle of Li/LiFePO<sub>4</sub> cells comparing cathodes with PVdF and WSB binders at 25 °C. The irreversible capacity loss was 8% with WSB compared to 11% with PVdF binder cathode. This difference is attributed to two factors: (i) WSB is a fluorine-free binder and (ii) the amount of the WSB

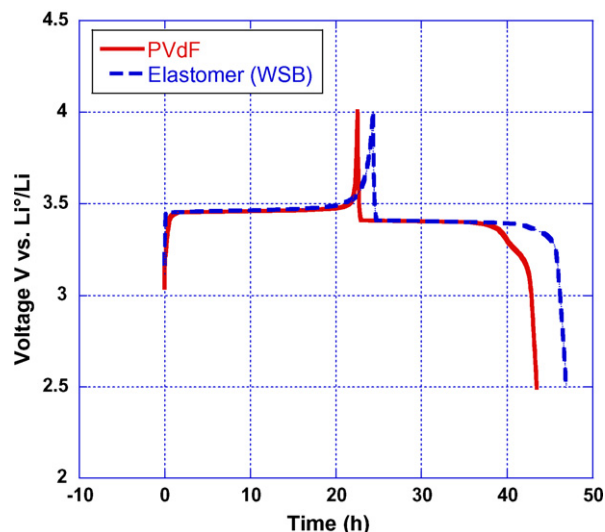


Fig. 7. First cycle of Li/LiFePO<sub>4</sub> cells comparing cathodes with PVdF and WSB binders at 25 °C at C/24.

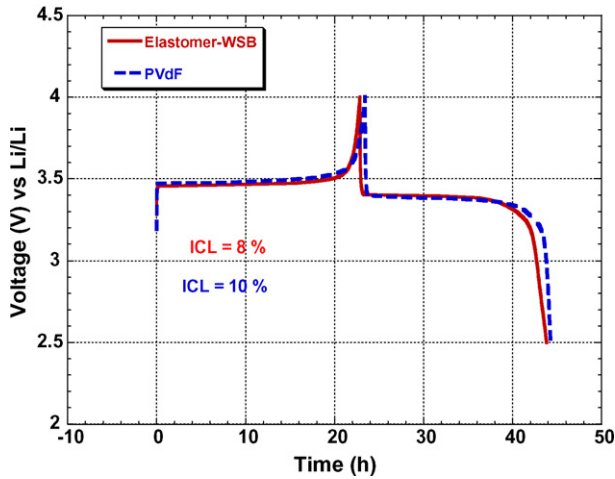


Fig. 8. First cycle of Li/LiFePO<sub>4</sub> cells comparing cathodes with PVdF and WSB binders at 60 °C at C/24.

used in the cathode is less than the amount of PVdF binder in the cathode.

In Li-ion battery applications, the battery must show acceptable performance at 60 °C, and thus we evaluated the LiFePO<sub>4</sub> with elastomer binder at this temperature. In Fig. 9, we show the cycle life of both cathodes prepared from PVdF and WSB evaluated at 60 °C under cycling at C/1 rate between 2.5 and 4.0 V. Both electrodes show a comparable performance at 60 °C and stable cycle life without any degradation of both binders. Based on this cycling test, both types of LiFePO<sub>4</sub> cathodes performed well at 60 °C. In the initial cycles, the capacity was increased with the cycle number, this phenomena is related to the coated carbon layer on LiFePO<sub>4</sub>. In order to complete the wettability of the carbon layer (with high surface area) a couple of cycles are needed to reach a stable capacity.

For long cycling life, the laminated type Li/LiFePO<sub>4</sub>-(WSB based) in EC-DMC-1 M LiPF<sub>6</sub> was adopted. Fig. 10 shows cycling life at C/1 discharging and C/6 charging rate at 60 °C. The capacity was maintained constant after 200 cycles at 135 mA<sub>g</sub> with 100% efficiency.

After 200 cycles, the high rate capability evaluation was performed on the cell. The discharge rates are obtained from

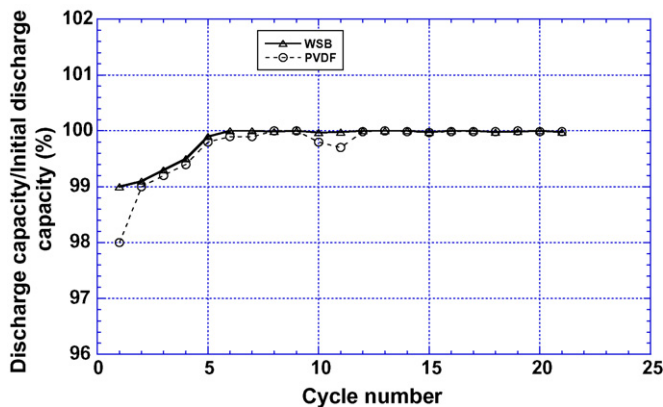


Fig. 9. Cycle life of cathodes prepared from PVdF and WSB evaluated at 60 °C at C/1 rate.

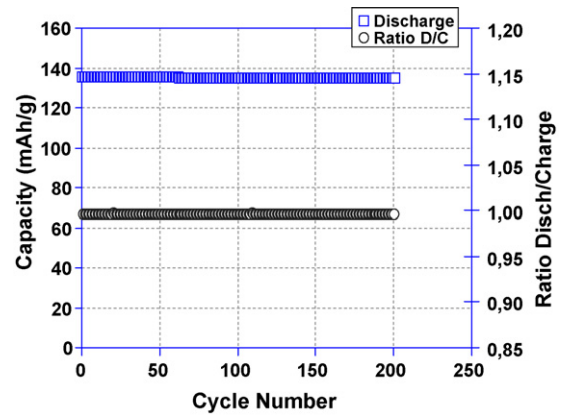
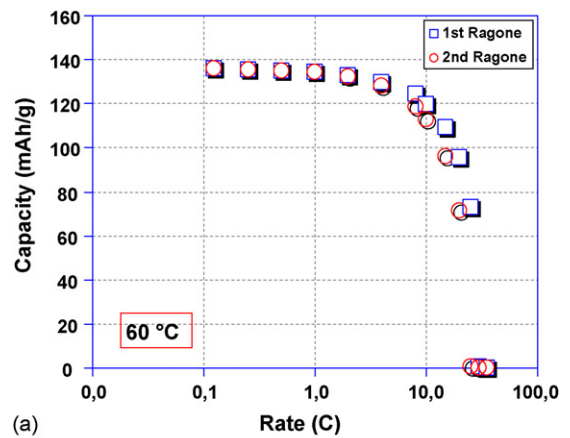
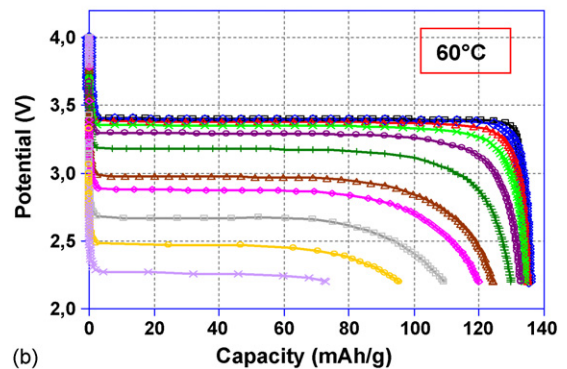
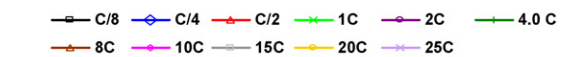


Fig. 10. Cycle life of Li/LiFePO<sub>4</sub> laminated cell with cathode prepared from WSB evaluated at 60 °C at C/1 rate.

the reversible capacity at C/24 rate. The cell was charged at fixed rate of C/6 and discharged at different rates from C/12 to 40C. In order to see the performance of the cell, a second Ragone test was followed after the cell was tested at high rate. Fig. 11a shows the Ragone plot at 60 °C of Li/LiFePO<sub>4</sub> cell. From C/12 to 6C rate, the capacity is almost maintained constant at 135 mA<sub>g</sub><sup>-1</sup>. From 6 to 25C the capacity decreases with increasing current density. The cell still has a good performance at 10C with 120 mA<sub>g</sub><sup>-1</sup> which represents 88% of the capacity



(a)



(b)

Fig. 11. Ragone plot of Li-ion LiFePO<sub>4</sub>/graphite laminated cell in EC-DEC-1 M LiPF<sub>6</sub> at 60 °C (a) and discharge curves at high rates (b).

at  $C/12$ . Even at discharge rate of  $15C$ , it remained over 80% of the capacity at  $C/12$ . The cell still delivers acceptable capacity at very high rate ( $25C$ ) with  $73 \text{ mAh g}^{-1}$ . The second Ragone test shows the same performance even after the cell was discharged at high rates.

The voltage profiles of  $\text{Li/LiFePO}_4$ - (WSB based) are shown in Fig. 11b at different discharge rates at  $60^\circ\text{C}$ . As the discharge current increases, the plateau voltage and the specific discharge capacity decreases. At  $C/8$ , the cell delivers  $136 \text{ mAh g}^{-1}$  with plateau at  $3.4 \text{ V}$  versus  $\text{Li/Li}^0$ . Until  $C/1$  the cell starts showing small displacement of the plateau to  $3.35 \text{ V}$ . At high rate ( $10C$ ), the cell delivers  $120 \text{ mAh g}^{-1}$  and the discharge curve has a plateau at  $2.88 \text{ V}$ . High polarization is shown at high rates due to the lack of conductivity at this level of rates.

#### 4. Conclusion

Our study indicates that fabrication of cathode coatings with low surface roughness is relatively easy to obtain with the ZEON elastomer water-soluble binder. These cathodes are much more flexible than cathodes based on PVdF cathode (by a factor 2). By using elastomer binder, the amount of binder was reduced while still maintaining better mechanical properties of the cathodes. The electrochemical performance shows lower irreversible capacity losses were obtained with cathodes with the elastomer binder. At  $60^\circ\text{C}$ , both binders show stable cycling life. The cell

shows high rate capability at  $60^\circ\text{C}$  with more than 80% of the capacity can be delivered at  $15C$ .

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