

# Improved composite materials for rechargeable lithium metal polymer batteries

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## Abstract

The performance of several polymer electrolytes for lithium metal batteries for electric vehicle applications are reported. The best performing electrolyte is the composite  $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3-\gamma\text{LiAlO}_2$ , which was prepared by a solvent-free procedure. It showed coulombic efficiency values of the lithium deposition–stripping process of 94%–96%. Electrochemical tests of lithium polymer battery (LPB) prototypes based on a 3 V  $\text{LiMn}_2\text{O}_4$  composite cathode material laminated together with the  $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3-\gamma\text{LiAlO}_2$  electrolyte gave promising results for electric vehicle applications. Even under non-optimized battery design, the prototypes delivered, at the C/3 rate and at 94°C, 40%–30% of theoretical capacity over 100 charge–discharge cycles. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Polymer electrolytes; Lithium interface; Manganese cathode; Lithium metal polymer batteries

## 1. Introduction

Given its high energy density, the lithium metal polymer battery (LPB) is the most promising answer to the demand for electric vehicle (EV) power supply [1]. Polymer electrolytes with ceramic filler show high lithium metal interface stability, leading to new perspectives in the development of these batteries [2]. Indeed, LPBs for EVs are the focus of Italy's ALPE project, which began in 1994 and involves two universities, a government energy agency and a private company. The 4-year project's brief is to develop low-cost materials by environment-friendly manufacturing methods. Several types of polymer electrolytes have been developed and tested: (i) ceramic-added polyethylene oxide (PEO)-based electrolytes prepared by dry procedure, (ii) plasticized composite PEO-based electrolytes and (iii) chemically cross-linked PEO-based electrolytes. Much effort has also been devoted to the preparation of a highly reversible composite cathode material based on  $\text{LiMn}_2\text{O}_4$  operating at 3 V vs. Li [3].

The results of the present study confirm that the high lithium interface stability of the dry composite polymer electrolyte and the 3 V cathode material, which keeps the battery operating within a safe electrochemical window of the electrolyte, lead to well-performing LPBs.

## 2. Experimental

### 2.1. Electrolyte preparation

The ceramic-added PEO-based electrolyte ( $\text{PEO}_{20}\text{-LiCF}_3\text{SO}_3-\gamma\text{LiAlO}_2$ ) was prepared by a dry procedure by mixing PEO,  $\text{LiCF}_3\text{SO}_3$  and  $\gamma\text{LiAlO}_2$  powders with the weight ratio 68:12:20. This mixture was extruded and calendered by a semiautomatic apparatus to yield polymer tapes 0.17 mm thick, 20 mm width and several meters long [4,5]. The laminated tapes were hot pressed at 110°C to relax the polymer chains.

The plasticized, composite PEO-based electrolyte ( $\text{PEO-PEGDME-LiCF}_3\text{SO}_3-\gamma\text{LiAlO}_2$ ) was prepared as reported in Ref. [6] and the chemically cross-linked PEO-based electrolyte ( $\text{PEG-PEGDME-LiCF}_3\text{SO}_3$ ) obtained as reported in Ref. [7].

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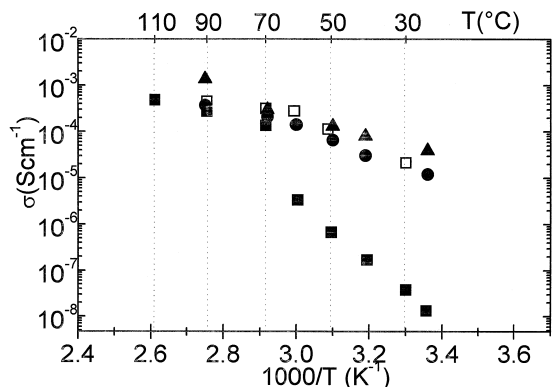


Fig. 1. Arrhenius plot of the  $\text{PEO}_{20}\text{LiSO}_3\text{CF}_3-\gamma\text{LiAlO}_2$  dry electrolyte (heating  $\blacksquare$ , cooling  $\square$ ), the  $\text{PEO}-\text{PEGDME}-\text{LiSO}_3\text{CF}_3-\gamma\text{LiAlO}_2$  plasticized electrolyte ( $\blacktriangle$ ) and the  $\text{PEG}-\text{PEGDME}-\text{LiSO}_3\text{CF}_3$  chemically crosslinked electrolyte ( $\bullet$ ).

## 2.2. Electrolyte characterisation

The ionic conductivity of the polymer films and the Li metal interface stability were evaluated by impedance spectroscopy using a 1255 Solartron frequency response analyzer coupled to a 273 PAR potentiostat/galvanostat, both PC interfaced. A 10 mV ac perturbation was used and the data were collected over a frequency range from 100 kHz to 1 Hz in conductivity measurements and from 100 kHz to 10 mHz in interface investigation by recording 10 points/decade. The impedance results were examined by Boukamp's fitting program [8]. The lithium current fraction was evaluated as reported in Refs. [6,7,9,10]. The efficiency of the lithium deposition–stripping process was evaluated on the  $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3-\gamma\text{LiAlO}_2$  electrolyte by repeated galvanostatic pulses at  $\pm 167 \mu\text{A cm}^{-2}$  on a lithium–lithium cell where the first electrode, laminated with the polymer electrolyte, was 5–8  $\mu\text{m}$  thick and the second 0.2 mm thick. The test was stopped when the voltage abruptly increased, indicating total consumption of the thinner lithium electrode. The value of the deposition–

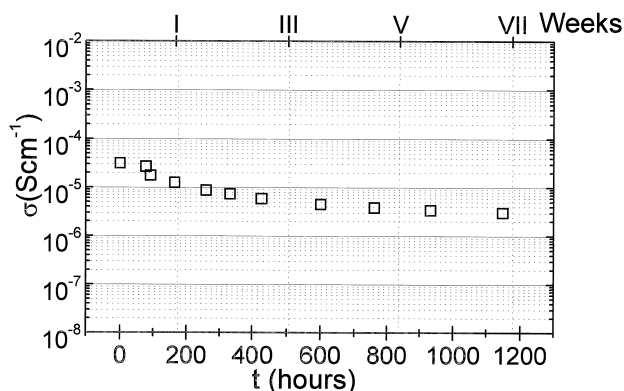


Fig. 2. Conductivity of the dry composite electrolyte  $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3-\gamma\text{AlO}_2$  during storage at  $30^{\circ}\text{C}$  after heating at  $110^{\circ}\text{C}$ .

stripping process efficiency ( $\eta$ ) was calculated by the equation

$$\eta = nQ_c / (nQ_c + Q_d) \times 100, \quad (1)$$

where  $n$  is the total number of cycles,  $Q_c$  the cycled charge ( $0.167 \text{ C cm}^{-2}$ ) and  $Q_d$  the capacity of the thinner electrode ( $3.7\text{--}6.0 \text{ C cm}^{-2}$ ). The equipment was a PC interfaced with a 273A PAR potentiostat/galvanostat.

## 2.3. $\text{LiMn}_2\text{O}_4$ cathode material and composite cathode preparation and characterization

Two kinds of  $\text{LiMn}_2\text{O}_4$  were prepared by dry reaction [11,12] of  $\text{Li}_2\text{CO}_3$  (Fluka, purum  $> 98\%$ ) and  $\gamma\text{MnO}_2$  (Fluka, activated  $> 88\%$ ) (yielding  $\text{LiMn}_2\text{O}_4$ , A) or  $\beta\text{MnO}_2$  (Fluka, puriss.  $\geq 99\%$ ) (yielding  $\text{LiMn}_2\text{O}_4$ , B) with the weight ratio 16:84. The dry reactions were performed by heating at  $450^{\circ}\text{C}$  for 24 h and cooling to room temperature for 5 h (six replicates).  $\text{LiMn}_2\text{O}_4$  (A) or (B), graphite (Aldrich) and Teflon, mixed at the weight ratio 75:10:15, were pressed at room temperature on a stainless-steel grid. The resulting electrodes, with about 4 C capacity, were galvanostatically charged and discharged in dry box at room temperature at C/10 rate in propylene carbonate (PC) 1 M  $\text{LiCF}_3\text{SO}_3$ .

The cathode for the LPBs was obtained by mixing  $\text{LiMn}_2\text{O}_4$  (A), carbon black (Ketjenblack—Akzo Nobel) and  $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$  at the weight ratio 60:5:35. The mixture was laminated and calendered together with the dry  $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3-\gamma\text{LiAlO}_2$  electrolyte (0.17 mm thick) to yield tapes 0.40 mm thick. LPB prototypes were assembled in dry box as flat, thin cells using a lithium foil anode (0.20 mm thick) and the cathode film laminated on to the dry composite polymer electrolyte. The performance of these prototypes was evaluated in dry box by galvanostatic

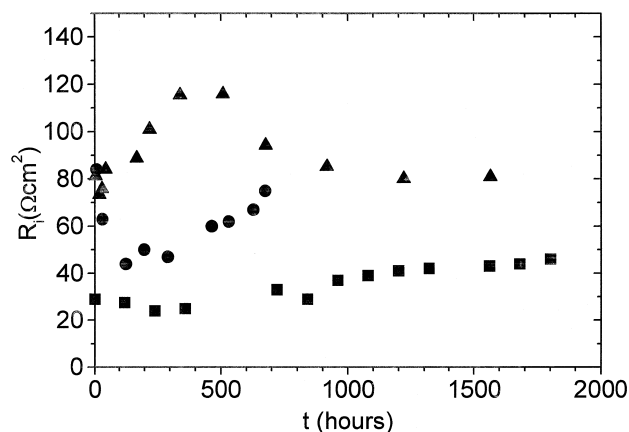


Fig. 3. Evolution over storage time at  $30^{\circ}\text{C}$  of the lithium metal/electrolyte interface resistance for the  $\text{PEO}_{20}\text{LiSO}_3\text{CF}_3-\gamma\text{LiAlO}_2$  dry electrolyte ( $\blacksquare$ ) at  $90^{\circ}\text{C}$ , the  $\text{PEO}-\text{PEGDME}-\text{LiSO}_3\text{CF}_3-\gamma\text{LiAlO}_2$  plasticized electrolyte ( $\blacktriangle$ ) at  $70^{\circ}\text{C}$  and the  $\text{PEG}-\text{PEGDME}-\text{LiSO}_3\text{CF}_3$  chemically cross-linked electrolyte ( $\bullet$ ) at  $70^{\circ}\text{C}$ .

Table 1

Composition and lithium current fraction of three classes of electrolytes: the dry composite PEO-based electrolyte, the plasticized composite PEO-based electrolyte and the cross-linked PEO-based electrolyte.

Class	Composition	$T^+$
Dry	PEO <sub>20</sub> LiSO <sub>3</sub> CF <sub>3</sub> - $\gamma$ LiAlO <sub>2</sub> (20% w/w), EO/Li = 20	0.35 (85°C)
Plasticized	PEO-PEGDME (1:4)-LiSO <sub>3</sub> CF <sub>3</sub> - $\gamma$ LiAlO <sub>2</sub> (5% w/w), EO/Li = 8	0.66 (70°C)
Cross-linked	PEG-PEGDME (1:1)-LiSO <sub>3</sub> CF <sub>3</sub> , EO/Li = 18	0.44 (90°C)

EO = ethylene oxide; PEG = polyethylene glycol, M.W. 2000; PEGDME = polyethylene glycol dimethyl ether, M.W. 500.

charge–discharge cycles just above 90°C to assure properly high electrolyte conductivity.

### 3. Results and discussion

Fig. 1 shows the temperature dependence of the conductivity of the three best-performing polymer electrolytes, each representing a different strategy to improve ionic conductivity. The dry PEO composite electrolyte reached a conductivity of  $10^{-4}$  S cm<sup>-1</sup> at 70°C, which was assumed as the lowest conductivity for EV battery application. The conductivity remained over  $10^{-5}$  S cm<sup>-1</sup> during the cooling step because of the slow recrystallization kinetics, as confirmed by the slight decrease of conductivity during storage at 30°C for more than 7 weeks (Fig. 2). During the heating step the conductivity of the plasticized and of the chemically cross-linked PEO electrolytes reached  $10^{-4}$  S

cm<sup>-1</sup> at 60°C, the conductivity values overlapping those of the first heating step during subsequent cooling. Fig. 3 shows the lithium/electrolyte interface resistance evolution over time at 90°C and 70°C for the three polymer electrolytes in storage condition at 30°C. For each of them the interface resistance values were almost constant over 1 month; the best performing was the dry PEO composite (PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>- $\gamma$ LiAlO<sub>2</sub>) electrolyte—presumably because of its liquid-free preparation—and it was maintained under test for a longer storage time. However, this electrolyte had the lowest lithium current fraction ( $T^+$ ), as Table 1 shows. The addition of plasticizer indeed increases the lithium current fraction even at higher lithium salt concentration. The steady-state current is related to the product  $\sigma T^+$  and a light rising of the operating temperature can lead to a conductivity value that offsets the relatively low value of  $T^+$ . The dry composite electrolyte was thus used to assemble the LPB prototypes. The

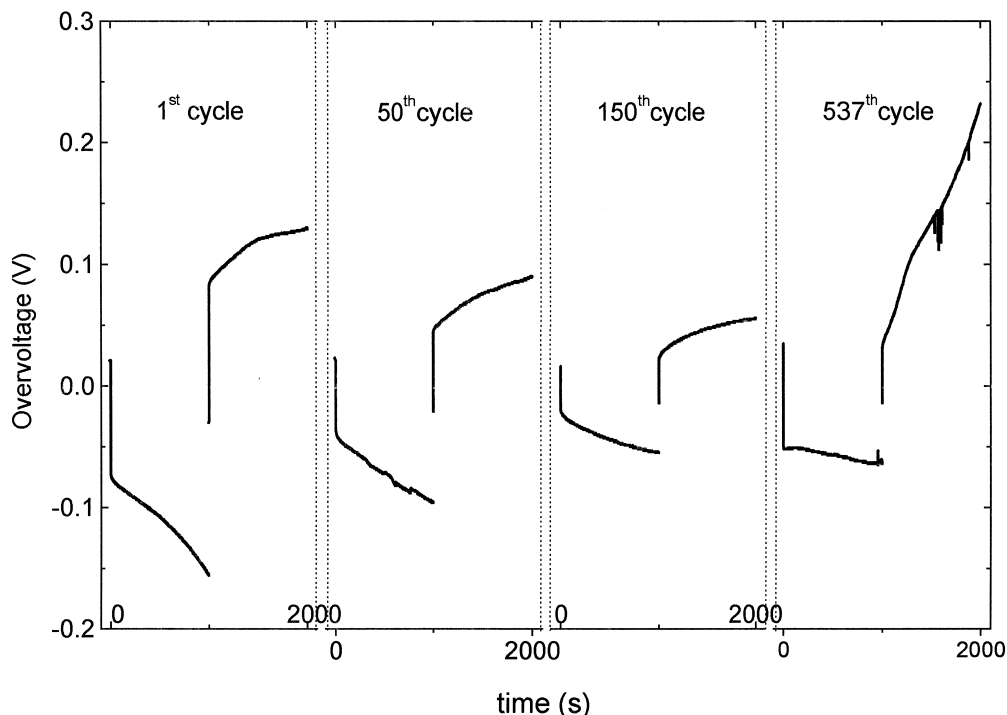


Fig. 4. Voltage profiles of deposition–stripping galvanostatic cycles at  $\pm 167 \mu\text{A cm}^{-2}$  and 90°C on a Li (5–8  $\mu\text{m}$  thick)/PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>- $\gamma$ AlO<sub>2</sub> (0.17 mm thick)/Li (0.20 mm thick) cell.

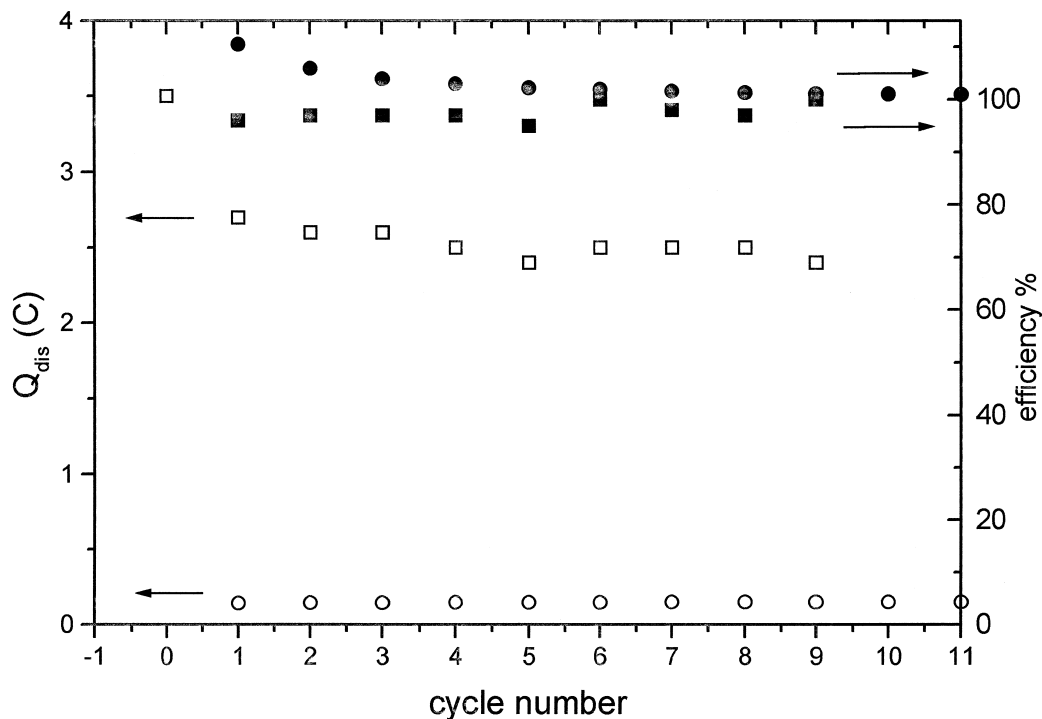


Fig. 5. Cyclability performance of the cathode materials based on LiMn<sub>2</sub>O<sub>4</sub> (A) and LiMn<sub>2</sub>O<sub>4</sub> (B) in dry box at room temperature at C/10 rate in propylenecarbonate (PC) 1 M LiCF<sub>3</sub>SO<sub>3</sub>. The results are reported as delivered cathode capacity ( $Q_{dis}$ ): □ LiMn<sub>2</sub>O<sub>4</sub> (A), ○ LiMn<sub>2</sub>O<sub>4</sub> (B); and coulombic efficiency: ■ LiMn<sub>2</sub>O<sub>4</sub> (A), ● LiMn<sub>2</sub>O<sub>4</sub> (B), vs. cycle number. Voltage limits: 2.5 V discharge and 3.5 V charge.

coulombic efficiency of the lithium deposition–stripping process on the dry composite electrolyte was also evaluated, and Fig. 4 shows the overvoltage profiles of repeated galvanostatic cycles run on a Li/PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>– $\gamma$ LiAlO<sub>2</sub>/Li cell with lithium electrodes of different thickness. The overvoltage decreased during the first cycles,

probably because of an electrochemical cleavage of the lithium electrode, and remained almost constant thereafter up to the 537<sup>o</sup> cycle, when a sharp increase of the stripping overvoltage indicated the total consumption of the thinner lithium electrode. The lithium deposition–stripping efficiency as calculated by Eq. (1) was  $\eta = 94\%–96\%$ , a

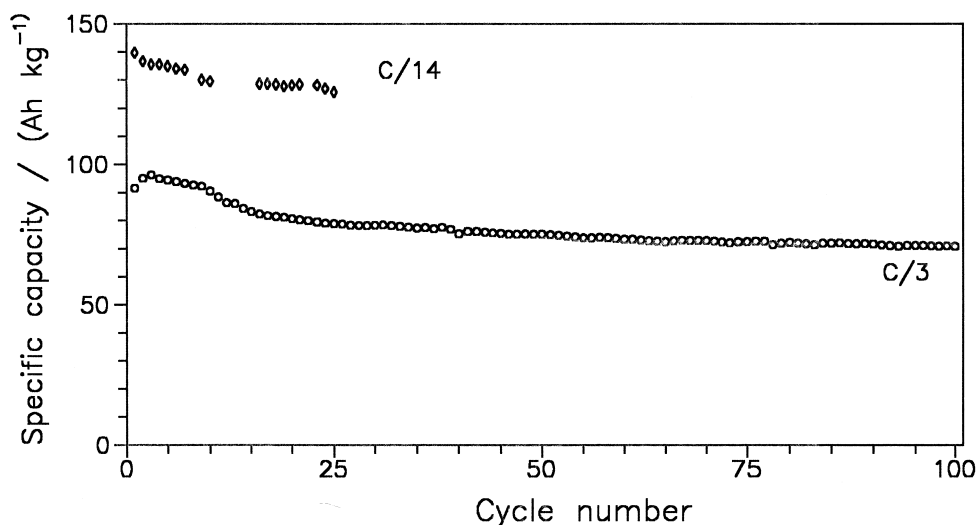


Fig. 6. Cyclability performance of the composite cathode based on LiMn<sub>2</sub>O<sub>4</sub> (A) in dry box at room temperature at C/14 and C/3 rate in propylenecarbonate (PC) 1 M LiClO<sub>4</sub>. The results are reported as specific cathode capacity vs. cycle number. Voltage limits: 2.5 V discharge and 3.5 V charge.

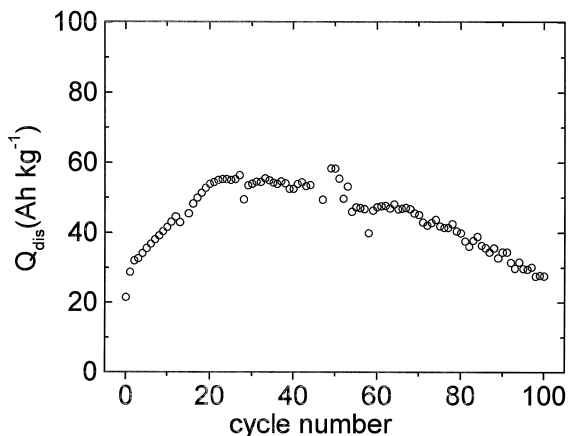


Fig. 7. Cyclability of a flat-type Li/PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>- $\gamma$ AlO<sub>2</sub>/LiMn<sub>2</sub>O<sub>4</sub> lithium polymer battery at 94°C and C/3 (0.64 mAcm<sup>-2</sup>) rate. The results are reported as delivered specific cathode capacity ( $Q_{\text{dis}}$ ) vs. cycle number. Voltage limits: 2.4 V discharge and 3.6 V charge. The battery prototype was not optimized for electrode material balance and thickness of the electrolyte.

promising value even if higher efficiency values need to be achieved to assure an LPB life of 600 cycles.

Fig. 5 displays the contrasting cyclability performance of the LiMn<sub>2</sub>O<sub>4</sub> (A) and LiMn<sub>2</sub>O<sub>4</sub> (B) cathode active materials tested in liquid electrolyte at C/10 rate. Their divergent responses are probably linked to the different structures of the MnO<sub>2</sub> precursors, and Fig. 6 shows the cyclability of the best performing LiMn<sub>2</sub>O<sub>4</sub> (A) electrode at C/14 and C/3.

Fig. 7 shows the cathode capacity delivered during the discharge ( $Q_{\text{dis}}$ ) vs. cycle number at 94°C and C/3 rate of a LPB prototype assembled with the LiMn<sub>2</sub>O<sub>4</sub> (A) as active cathode material. The battery cycled the 40–30% of the theoretical 140 A h kg<sup>-1</sup> value. Thus, for electrode material balance and electrolyte thickness, the energy density of the battery (based on the weight of electrode active materials, cell capacity and average cell voltage) is of the order of 130 W h kg<sup>-1</sup>. It is also important to point out that the results in Fig. 7 show that the amount of delivered

capacity is reasonably stable upon 100 cycles, with a charge–discharge efficiency approaching 100%. Such cycling stability is uncommon and it is related to the improved interface stability between the dry, ceramic-added composite electrolyte and the lithium metal electrode.

#### 4. Conclusion

The results of this study indicate that the PEO<sub>20</sub>-LiSO<sub>3</sub>CF<sub>3</sub>- $\gamma$ LiAlO<sub>2</sub> prepared by a solvent free procedure is a very promising polymer electrolyte for the development of LPBs for EVs.

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