

Short communication

# Composite gel-type polymer electrolytes for advanced, rechargeable lithium batteries

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## Abstract

The main goal of this work was to determine whether the dispersion of ceramic fillers have any promotion effect on the properties of solid-like, gel-type lithium conducting polymer electrolytes. Using a series of different but complementary techniques, which included SEM analysis, voltammetry and impedance spectroscopy, we demonstrate that the dispersion of surface functionalized fumed silica and alumina, respectively, to PVdF–carbonate solvent–lithium salt systems, while not greatly influencing the transport properties, does stabilize the lithium metal interface and the mechanical properties of the resulting composite GPE electrolytes. The relevance of these features in view of practical application is here demonstrated by the response of lithium batteries based on selected GPEs.

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**Keywords:** Polymer; Poly(vinylidene fluoride); Electrolytes; Lithium; Battery

## 1. Introduction

Gel polymer electrolyte (GPE) membranes are well known separators in lithium electrochemical devices and accordingly, many types have been developed and characterized in various academic and industrial laboratories [1–3]. Our laboratory from many years has focused particular attention on poly(vinylidene fluoride) PVdF based systems, gelled in alkylcarbonate solvents like ethylene carbonate (EC) and propylene carbonate (PC) [4,5]. The applicability of gel electrolytes in lithium and lithium-ion batteries has been clearly demonstrate by us and by others [6–8].

In comparison to common liquid electrolytes, the most appealing feature of gel membranes is the free standing consistency that allows easy handling and cell design, modularity and reliability. Respect other solid polymer electrolytes, like PEO-based ones [9], the gel electrolytes have the great advantage of offering high conductivity, i.e. of the order of  $10^{-3}$  S cm<sup>-1</sup>, over a wide temperature range, combined with a large and a wide

electrochemical stability, i.e. extending up to 5 V versus Li<sup>+</sup>/Li [10].

However, although largely studied, gel-type electrolytes are still open to improvement. Areas which still need attention are: (i) integrity, i.e. capability of liquid retention and (ii) interfacial stability, e.g. with the lithium metal electrode. It has been largely demonstrated that addition of appropriate ceramic fillers to PEO-based membranes gives rise to composite polymer electrolytes with enhanced transport and interfacial properties [11]. Although this approach can in principle be extended to any class of electrolytes, no many studies have been so far reported for the case of gel-type systems. However, the results, although limited to few examples, demonstrates that the dispersion of ceramic fillers does improve the interfacial properties. Relevant in this respect is the work by Fedkiw and co-workers who showed that the addition of fumed silica powders in low molecular weight poly(ethylene oxide) ethers, resulted in the formation of liquid-type, composite polymer electrolytes having stable interfacial properties [12,13].

In this work we extend the composite approach to solid-like, gel-type electrolytes. We demonstrate that the dispersion of surface functionalized fumed silica and alumina, respectively to PVdF–carbonate solvent–lithium salt systems, while

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not greatly influencing the transport properties, does stabilize the lithium metal interface of the resulting composite electrolytes.

## 2. Experimental

Non conductive, precursor composite membranes were prepared by a two-step casting procedure originally developed in our laboratory [4–6,14]. The composition of these membranes was: 18% PVdF (Solvay Solef UHMW 6020) + 80% EC-PC (1:1 by wt.) (Merck Selectipur, Battery Grade) + 2% filler. Fumed  $\text{SiO}_2$  (Aldrich) and  $\text{Al}_2\text{O}_3$  (Aldrich) in its acid,

neutral and basic states, respectively were the fillers of choice. The scale of acidity of the surface groups of these ceramic was estimated by simply measuring the pH of related water dispersions, as  $\text{SiO}_2 \gg \text{acid Al}_2\text{O}_3 > \text{neutral Al}_2\text{O}_3 \gg \text{basic Al}_2\text{O}_3$ . Before use, silica was thermally treated at  $950^\circ\text{C}$  under argon flux in order to clean the surface from carbonates, neutral and basic alumina were treated under vacuum at respectively  $130^\circ\text{C}$  and  $200^\circ\text{C}$ , respectively to eliminate adsorbed water, while acid alumina was used as purchased.

The precursor membranes were then activated by immersion in a 1 M  $\text{LiClO}_4$  (Merck Selectipur, Battery Grade) EC:PC (1:1) solution, this inducing the desired lithium transport for poly-

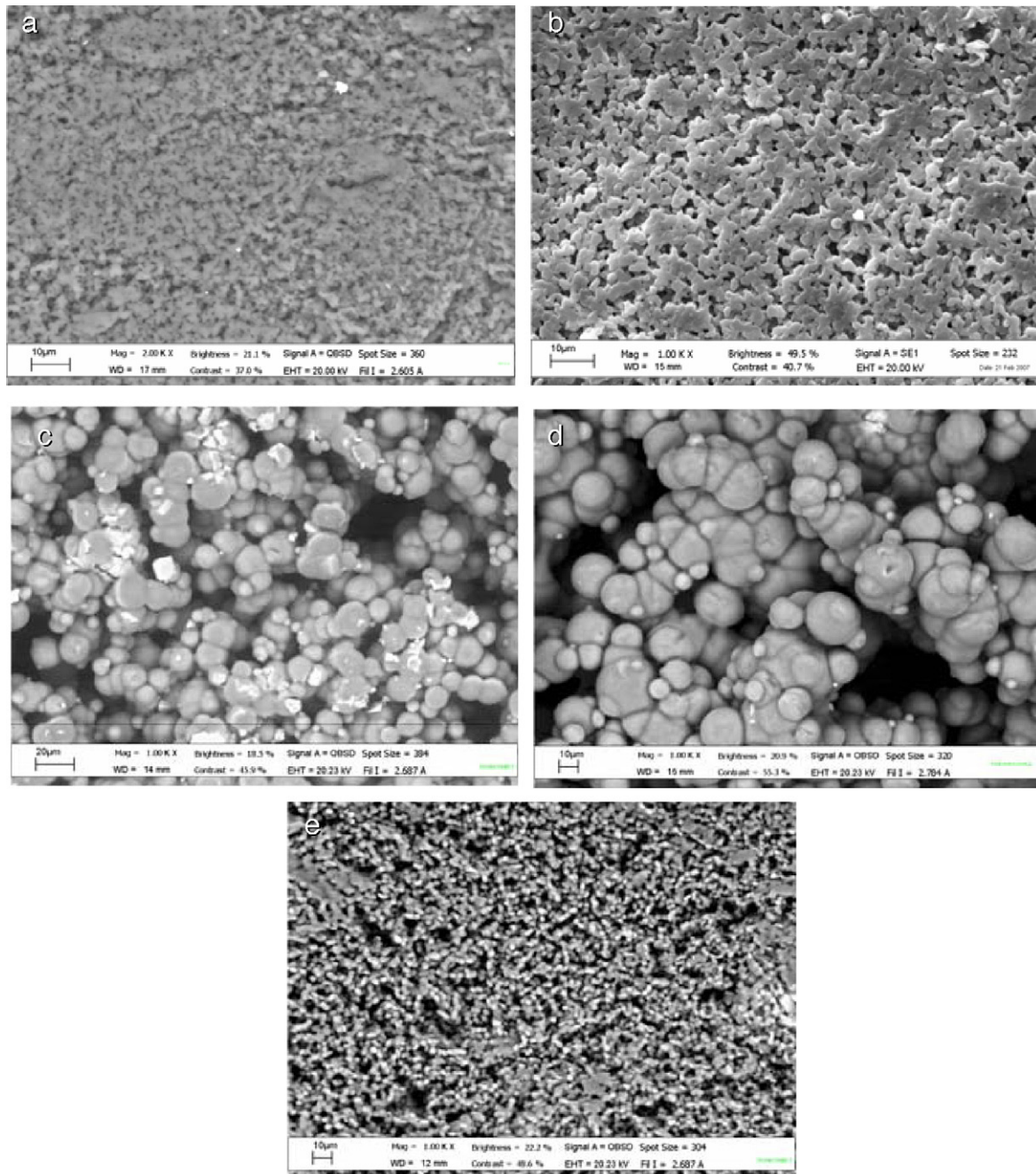


Fig. 1. SEM images of the various gel polymer electrolytes (GPEs) samples prepared in this work: (a) filler free GPE; (b) GPE +  $\text{SiO}_2$ ; (c) GPE + basic  $\text{Al}_2\text{O}_3$ ; (d) GPE + neutral  $\text{Al}_2\text{O}_3$ ; (e) GPE + acid  $\text{Al}_2\text{O}_3$ .

mer electrolyte application. Storage and activation of membrane occurred at room temperature.

The morphology of the membranes was determined by scanning electron microscopy SEM, using a Leo EVO 40 apparatus. The conductivity of the activated gel electrolyte membrane was measured by impedance spectroscopy ( $1 \times 10^5$  to 1 Hz,  $\Delta V = 10$  mV, Solatron model 1260) of two blocking electrode cells. The anodic breakdown potential was determined by running a linear scan voltammetry ( $0.1 \text{ mV s}^{-1}$  scan rate, PAR 362 potentiostat) in a cell having a lithium metal counter electrode, a large specific surface area Super P carbon working electrode and the given membrane as the electrolyte. The lithium metal electrode interfacial properties were investigated by impedance spectroscopy run on symmetric lithium/gel polymer electrolyte/lithium cells. The measurements were performed during 30 days, by applying a 10 mV amplitude signal in the  $5 \times 10^4$  to  $1 \times 10^{-3}$  Hz frequency region. Least square refinement of impedance spectra were carried out by the Ecvircirt software developed by Boukamp [15]. The lithium polymer batteries were assembled using the given gel polymer electrolyte a separator and a  $\text{LiFePO}_4$ -based positive electrode, kindly provided by Dr. Wohlfahrt-Mehrens at the Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) in Ulm, Germany [16]. To prepare electrodes,  $\text{LiFePO}_4$  was mixed to 10% Super P carbon additive and to 5% PVdF binder; the mixture was dispersed into *N*-methyl-2-pyrrolidinone then cast to aluminium foil and 10 mm diameter disks were cut. The galvanostatic charge–discharge cycles were carried out by a Maccor battery test system.

Unless specified, all electrochemical measurements were performed at room temperature.

### 3. Results and discussion

The gel polymer electrolyte (GPE) membranes prepared in this work have a plastic-like, free standing consistency and look homogeneous, colourless but opalescent. Their typical thickness averaged around 1–1.5 mm.

Fig. 1a–e shows SEM images of the various salt free GPE samples studied in this work. To be noticed that all the samples were previously dried under vacuum for 12 h in order to get rid of the solvents. The comparison between Fig. 1a, which refers to a filler-free sample, and all the others, which refer to various composite samples, evidences the changes in morphology induced by the dispersion of the ceramic. Indeed, the ceramic-free membrane reveals a sponge-like, homogeneous and continuous microporosity (Fig. 1a), while the composite membranes appear as formed of aggregates of micrometric spherical particles with a large porosity (Fig. 1b–e). Differences in particle diameters may be probably attributed to differences in ceramic size.

Considering the above-discussed difference in morphology, one can assume that the filler particles act as nucleation and growth centres for the polymer chains during the gelling procedure. The continuity of the membrane is granted by the sharing of the polymer chains of more than one aggregate.

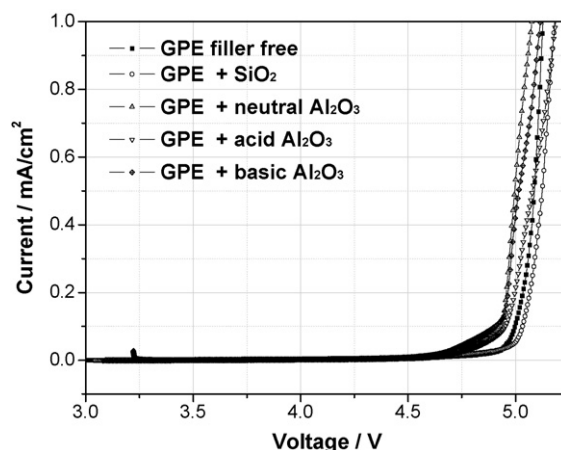


Fig. 2. Anodic scan on Super P working electrode. Scan rate:  $0.1 \text{ mV s}^{-1}$ . Room temperature.

Fig. 2 shows the current–voltage curves of a Super P working electrode in cells using lithium metal as counter and as reference electrode and varying by the electrolyte, which changed from a filler-free GPE to progressively each of the composite GPEs developed in this work. The ongoing of the current identifies the anodic decomposition voltage of the electrolytes. To be noticed that this anodic limit does not vary much passing from one cell to the others, being generally set around 5 V versus Li. This in turn shows that the fillers have no influence in the decomposition of the GPEs, with the possible exception of  $\text{Al}_2\text{O}_3$ . In fact, the alumina-added GPEs seem to decompose slightly before the 5 V associated to the filler-free GPE, this suggesting a certain catalytic effect of the filler. In any case, the difference is almost negligible and thus, not worth of speculations.

Fig. 3a and b shows the conductivity Arrhenius plots of the various GPE samples developed in this work. To be noticed that all the samples have comparable conductivity values in the medium-low temperature range and thus, that the filler does not enhance the transport properties of the GPEs, as instead it is the case for PEO-based electrolytes [17,18]. This was not unexpected since the two systems are quite different in terms of structure and morphology. The PEO-based electrolytes have a structure formed by amorphous regions imbedded in large crystalline domains. In this case the ion transport requires flexibility of the polymer chains, which is typical of the amorphous state [17,18]. The fillers promote amorphicity and this explains their conductivity enhancement action in PEO-based electrolytes. Quite different is the situation in the gel polymer electrolytes here considered where the conductivity is due to the liquid component without any contribution or constrain from the polymer component. It is then clear that the filler cannot exert transport promotion action in this type of composite materials. However, a significant effect does occur in the high temperature range. Fig. 3a shows that above  $70^\circ\text{C}$  the conductivity of the filler-free GPE dramatically decays, and this is associated to the fact that at this temperature the polymer melts and thus, the membrane loses its consistence. Much more stable is the behaviour of the composite GPEs, whose conductivity remains stable and reproducible even at temperatures as high as  $90^\circ\text{C}$  (see Fig. 3a and

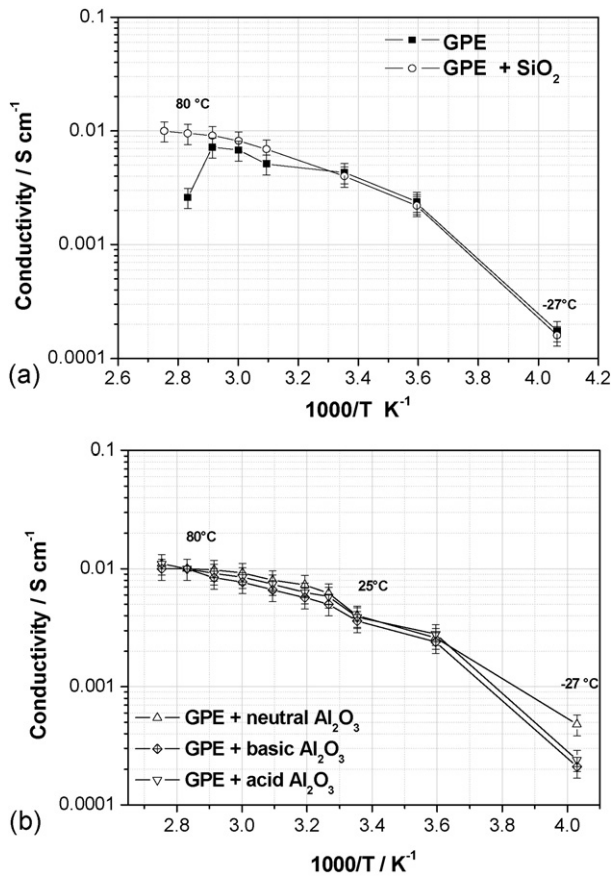


Fig. 3. Arrhenius plots for filler free GPE and SiO<sub>2</sub>-added GPE (a) and for Al<sub>2</sub>O<sub>3</sub> added GPE (b).

b). We may then assume that the filler, by limiting the fluidity of the polymer, consistently increases the mechanical stability of the GPEs, making them suitable for high temperature operation. This is one of the important effects promoted by the ceramic filler, which may have important practical implications, see further on.

Literature work, especially by Fedkiw and co-workers [12,13] showed that the addition of ceramic fillers, in that case fumed silica, consistently improve the interfacial properties of gel-type polymer electrolytes, in that case low molecular weight poly(ethylene oxide) ethers-based systems. This is another important effect, worth to be checked also for solid-like, GPEs examined in this work.

In order to study the behaviour of the lithium/GPE interphase, five symmetric Li/GPE/Li cells, where GPE was the filler free one and those containing SiO<sub>2</sub>, neutral, basic and acid Al<sub>2</sub>O<sub>3</sub>, respectively, have been assembled, and their impedance followed over time. The impedance response was practically similar for all cells and here we report that of two typical examples, i.e. the cell based on a ceramic-free GPE (Fig. 4a and b), and the cell based on a basic Al<sub>2</sub>O<sub>3</sub>-added, composite GPE (Fig. 5a and b). The Nyquist plots may be in both cases interpreted on the basis of a large depressed semicircle at high to medium frequency (50 kHz–0.5 Hz) and a badly defined small semicircle at low frequency (0.5 Hz–10 mHz).

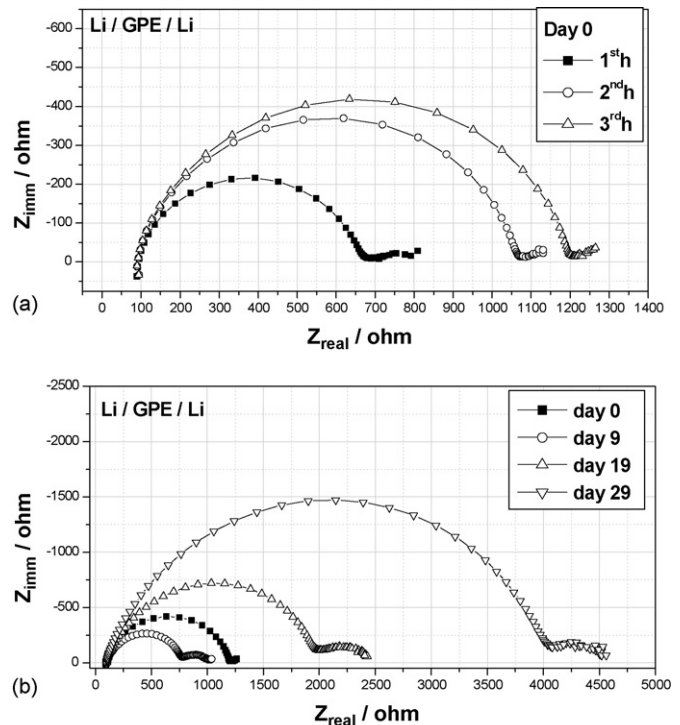


Fig. 4. Nyquist plots obtained for a symmetrical Li/filler-free GPE stored for 3 h (a) and for 1 month (b). Room temperature.

The high frequency semicircle may be associated to surface film layers combined with charge transfer kinetics [19,20]. Previous work by Aurbach and Zaban on alkyl carbonates liquid electrolytes [19], evidenced the formation of a surface film and

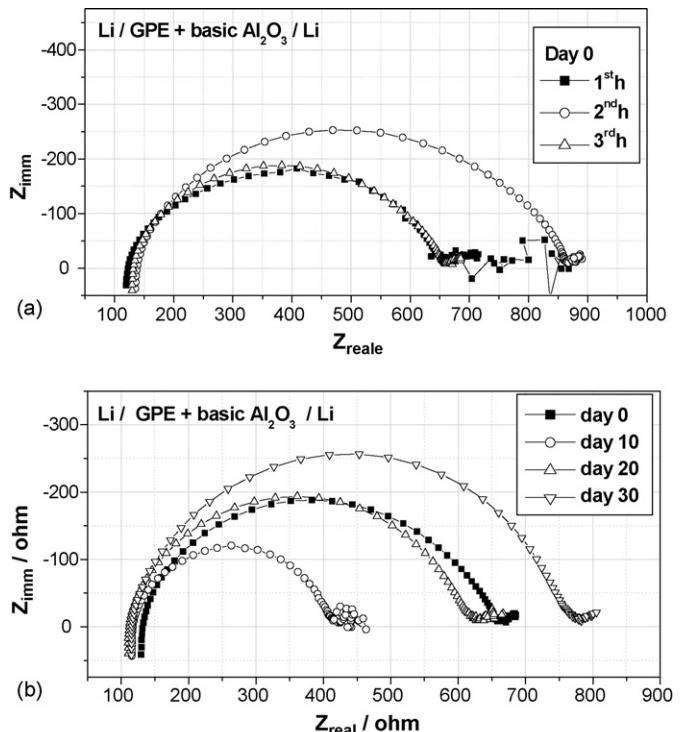


Fig. 5. Nyquist plots obtained for a symmetrical Li/composite GPE + basic alumina stored for 3 h (a) and for 1 month (b). Room temperature.

assumed that it had a complex and non homogeneous multilayer morphology. These authors also showed that such a multilayered film could be interpreted by a complex equivalent circuit based on series of RC parallels [19]. A similar multilayered film formation is also possible in the case of the GPEs studied in this work. The occurrence of a depressed semicircle may be index of the convolution of the two involved phenomena, i.e. the multilayered surface film and the charge transfer kinetics. Such convolution cannot be easily solved because of the closeness of time constants and we have fit the semicircle with a parallel of a resistance, representing the main overall resistance offered by the interface, and adding a constant phase element instead of a pure capacity.

Relatively simpler is the interpretation of the low frequency semicircle, which may be quite likely associated to finite length diffusion phenomena on a non blocking electrode.

The most relevant result of this impedance study is in the difference observed in the response of the ceramic-free GPEs-based cell in respect to that of cells based on composite GPEs. In the former case the amplitude of the main semicircle, as well as the  $\omega_{\max}$  and the degree of depression, considerably increase during storage time. The widening of the semicircle clearly demonstrates the growth of the interphase resistance and thus of the surface film. It is interesting to note that, as the semicircle becomes more depressed, the separation between the various time constants gets more pronounced, this suggesting also a modification upon time of the physical properties of the films. A similar modification was noticed by Aurbach and Zaban [19] and it was associated to the precipitation and dissolution equilibria of all the species constituting the multilayered film, thus producing an inner series of more compact layers and an outer porous layer with an high area surface. A similar explanation may also hold for the GPEs here investigated. Much more reduced are the changes observed for ceramic filler-added, composite GPEs.

Fig. 6 reports the time evolution trend of the interface resistance for all the Li/GPEs systems under investigation. In few hours, the interphase Li/filler-free GPE assumed a very high resistance, i.e.  $>1\text{ k}\Omega$ . Upon long storage time, the resistance underwent to important fluctuations, to finally reach a value exceeding  $4\text{ k}\Omega$  after 1 month. This was not a surprising behaviour since the surface film is expected to have a sort of dynamic evolution, that implies growing stages followed by

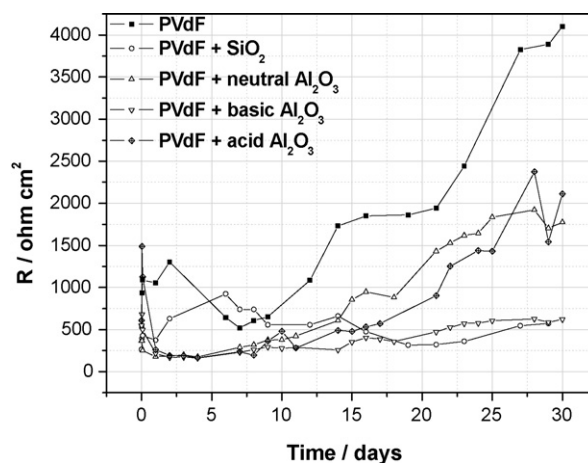


Fig. 6. Variation of the resistance of Li/GPE interface as a function of storage time at room temperature.

partial dissolution, growth again and occasional brake down due to thermal or mechanical stresses.

It appears evident from Fig. 6 that, in contrast to the above-discussed case of the ceramic-free GPE, the growth of the resistance of the Li/composite GPEs is characterized by much slower and more stable trend. This confirms that the disperse ceramics do improve the interfacial properties of the GPE. It is very interesting to observe that this stabilizing effect is higher in those systems containing silica and basic alumina, where the interphase resistance is limited to few hundreds of ohms. This suggests that not only the filler by itself, but also its surface groups may play a role in the stabilization of the interface with the attainment of a good passivating film. Silica and basic alumina are the ceramic with the more extreme pH values. Thus it is reasonable to assume that: a strongly acid or a strongly alkaline environment may both contribute, with different mechanisms, to produce suitable surface film.

Although further investigation is certainly needed to confirm this hypothesis, we may safely state that the stabilization of the electrode interface is a general, positive effect of the dispersed ceramic. The promotion of the interfacial stability, in combination with the already discussed enhancement of the mechanical properties, are important improvements in view of practical applications, since they may allow the use of composite

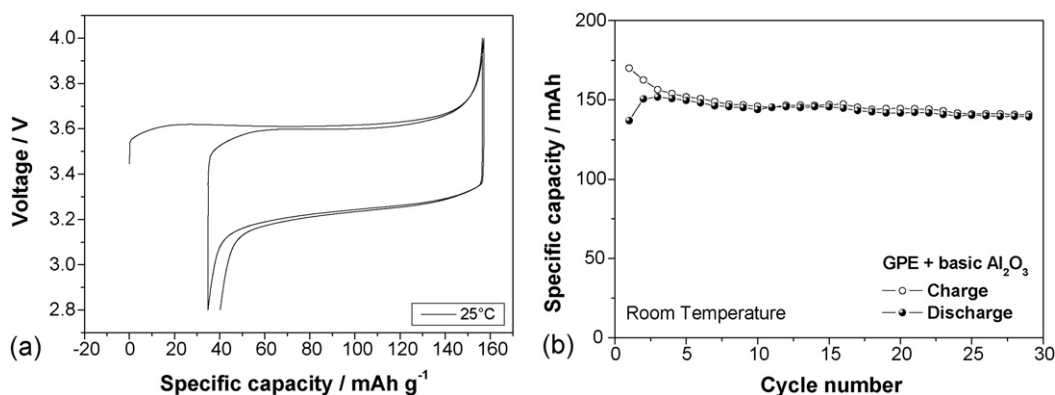


Fig. 7. Charge–discharge voltage profile (a) and capacity vs. cycle number of a Li/basic  $\text{Al}_2\text{O}_3$ -added GPE/LiFePO<sub>4</sub> (b) at 25 °C. Current rate C/5.

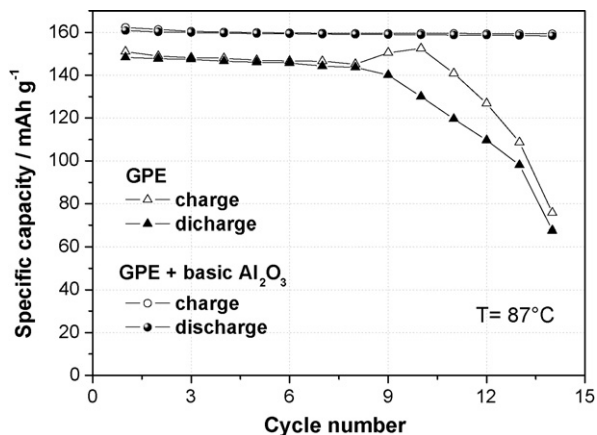


Fig. 8. Capacity vs. cycle number of a Li/basic Al<sub>2</sub>O<sub>3</sub>-added GPE/LiFePO<sub>4</sub> compared to Li/filler free GPE/LiFePO<sub>4</sub> at 87 °C. Current rate C/5.

GPEs in advanced rechargeable lithium batteries characterized by a long cycle life and by a high temperature operation.

To confirm this prevision, we have assembled and tested a lithium battery prototype. In consideration of its very good lithium interface properties (see Fig. 6), the composite, basic Al<sub>2</sub>O<sub>3</sub>-added GPE has been selected as the electrolyte of choice, while lithium iron phosphate, LiFePO<sub>4</sub> has been selected as cathode. The battery operates on the two-phase reversible process:



to which is associated a voltage of 3.4 V, i.e. compatible with the stability of the electrolyte, see Fig. 2, and a theoretical specific capacity of 170 Ah kg<sup>-1</sup> [21].

Fig. 7a which shows typical voltage profiles of this battery at 25 °C, reveals a difference between charge and discharge, this probably due to an ohmic overvoltage associated to the thickness of the GPE membrane, although kinetics limitations due to the poor electronic conductivity of the LiFePO<sub>4</sub> cannot be excluded. These losses contribute to reduce the specific capacity to a value of ca. 140 Ah g<sup>-1</sup>, i.e. about 80% of the theoretical. We are confident that this value can be considerably raised by optimizing the battery in terms of electrolyte thickness and cathode configuration. Fig. 7b shows the cycling response of the battery in terms of capacity versus cycle number. The capacity is stable and, particularly, the charge–discharge efficiency approaches 100% over all the testing range. The latter is a very convincing demonstration of a smooth lithium electrode interface characterized by a thin and stable surface film which prevents irregular, dendritic depositions upon charge, as in fact that expected to be promoted by the dispersed ceramic filler.

The other important effect of the filler is the enhancement of the mechanical stability at high temperature of the GPE (see Fig. 3). Thus batteries based on composite GPEs are expected to operate at temperatures, i.e. of the order of 80–90 °C, which are prevented for batteries using standard, ceramic-free GPEs. This is demonstrated in Fig. 8 which shows in comparison the cycling behaviour at 87 °C of the two batteries, with the filler free and the basic Al<sub>2</sub>O<sub>3</sub>-added GPEs as separator. The former fails after a very small number of cycles while the latter can be charged and discharged repeatedly without any capacity fade.

## 4. Conclusion

In this work we have shown that the dispersion of suitable ceramic fillers in solid-like, PVdF based gel polymer electrolytes gives rise to composite GPEs having some important specific properties. In fact, while not influencing the transport properties, the fillers do enhance the mechanical stability and, particularly the lithium interfacial properties of these composite GPEs, making them of practical interest for the development of advanced, rechargeable lithium batteries. The stabilization of the interface, reflecting in a smooth, stable lithium passivation film, prevents irregular, dendritic depositions upon charge, this finally allowing long and efficient cycling of the battery. The enhancement of the mechanical stability allows operation at temperature levels which cannot be stand by batteries using conventional, ceramic-free GPEs. Both these features have been confirmed and demonstrated in this work.

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