



Short communication

In-situ gelled electrolyte for lithium battery: Electrochemical and Raman characterization



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HIGHLIGHTS

- Polymer lithium cell using a PVdF-based, gel-type electrolyte is reported.
- The gel electrolyte is formed in-situ during cell assembly.
- Electrochemical impedance and Raman spectroscopy are used for electrolyte study.
- The polymer lithium cell is prepared using $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, spinel-type cathode.
- The cell is characterized by high voltage, good stability and high safety content.

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ABSTRACT

In this paper we report a polymer lithium cell using a PVdF-based, gel-type electrolyte formed in-situ during cell assembly. The gel electrolyte formation is monitored prior to cell assembly by electrochemical impedance spectroscopy and by Raman spectroscopy in order to determine the characteristics of the lithium salt diffusion into the gel-membrane. The results show an efficient gel formation and a fast lithium salt diffusion, this finally resulting in an optimized behaviour in a lithium cell using a high voltage spinel-type cathode. We believe that the results here reported may contribute to the enhancement of the safety of lithium batteries.

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1. Introduction

Lithium ion batteries are now triggering great attention since they are considered the most suitable power source for electric and hybrid vehicles [1]. However, the safety issues associated with the presence of organic, flammable solvents as the electrolyte are still preventing a large diffusion of the technology in these emerging markets [2]. Solid polymer electrolytes, such as polyethylene oxide (PEO), are considered the best choice to overcome the safety hazards, however problems associated with their low conductivity at

lower temperature still need to be addressed [3]. A very promising alternative was represented by the gelified systems, such as those based on poly(vinylidene)fluoride (PVdF), consisting of a polymer membrane acting as matrix for the organic liquid part, generally organic carbonates [4]. This solution was considered as a compromise between safety and performances in terms of ionic conductivity and rate capability when employed in lithium cells [5].

Different approaches have been taken in the past to prepare PVdF gel-type conducting membranes, such as those based on casting procedures [6] or on electro-spinning [7]. For both methods a swelling step is necessary to introduce a lithium salt into the membrane. However, these approaches revealed several issues associated with cell assembly and scaling up due to the poor mechanical stability of the gel membranes, in particular in roll-to-roll

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Table 1
Conditions used for the preparation of the gel electrolyte.

	Temperature, °C	Time
Mixing	Room temperature	2 h
Pre-heating	70	15 min
Casting	70	20 min
Quenching	Room temperature	20 min

systems, commonly used for cell prototype preparation. To overcome this issue, in this paper we report an alternative preparation approach consisting of an “in-situ” formation of the gel matrix during lithium-metal cell assembly, followed by the lithium salt infiltration step. The lithium salt diffusion into the gel is investigated by electrochemical impedance spectroscopy (EIS) and by Raman spectroscopy. The results demonstrated an efficient gel formation and a fast salt infiltration that allowed the use of the membrane in a lithium cell using a spinel-structure, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ high voltage cathode. It is expected that the procedure reported here may lead to the in-situ gel preparation also in full cell systems, combining both lithium ion cathode and anode, with the aim to increase the cell safety. In addition, the in-situ gelation procedure proposed may be successfully extended to a large variety of different applications, mainly to solve problems related to possible leakage of active components or analytical species. For example, drawbacks in the instrumental setup of some particular analyses, such as those based on in-situ spectroscopy or X-ray diffraction techniques, could be overcome by adopting a gelled configuration, to be easily realized in-situ, in order to avoid the presence of free liquids.

2. Experimental

2.1. Gel polymer electrolyte preparation and characterization

A membrane having the desired composition was prepared ex-situ by adapting a solvent casting procedure already developed in our laboratories [4]. The preparation of this membrane was aimed to fully investigate its characteristics prior to in-situ gel formation. Two low molecular weight aprotic solvents, ethylene carbonate (EC, Merck battery grade, 99.9%) and dimethyl carbonate (DMC, Merck battery grade, 99.9%) in a weight ratio of 1:1, were mixed with poly(vinylidene)fluoride (PVdF Solvay Solef® 6020). Details on the

preparation procedure of the gel polymer membrane are reported in Table 1. The final composition of the membrane was: EC:DMC/PVdF 80/20 wt/wt.

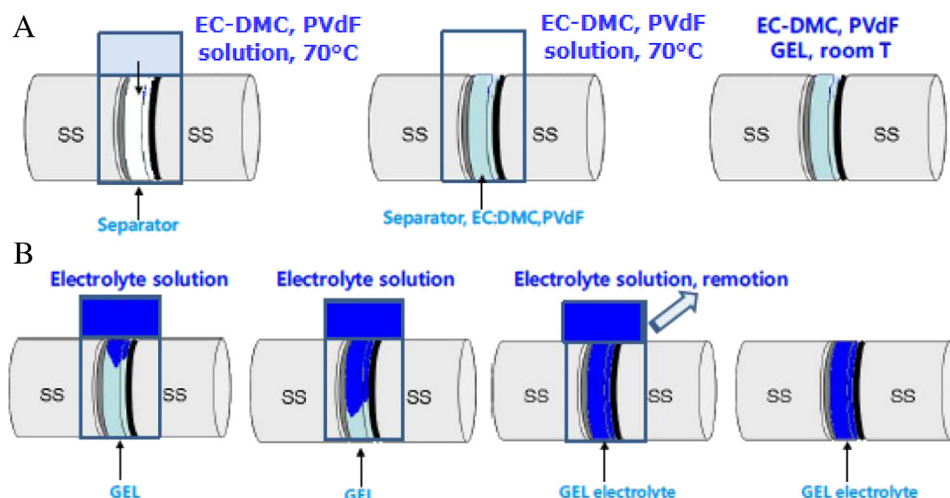
The as-prepared gel polymer membrane having a thickness of about 500 μm was held in a Swagelok, stainless steel electrode T-cell with geometric surface area of 0.785 cm^2 and infiltrated with the Li-salt from a solution of 1 M lithium hexafluorophosphate (LiPF_6) in EC:DMC 1:1 wt/wt, (LP30, Merck) for various time regimes at room temperature. This approach was adopted to preliminarily verify the applicability of in-situ activation and gel polymer electrolyte formation.

The ionic conductivity of the membrane during LiPF_6 infiltration was monitored by AC impedance (cell constant calculated to be 0.065 cm^{-1} in the configuration adopted). The impedance measurements were performed applying a 10 mV amplitude signal in the 100 kHz–100 Hz frequency range using a frequency response analyzer (FRA) Schlumberger Solartron model 1260.

The effective occurrence of LiPF_6 infiltration was also monitored by Raman spectroscopy, which allowed the determination of the lithium salt content. The analysis was performed in a sealed glass cuvette containing a LP30:gel membrane 2:1 v:v ratio. The dimensions of the cuvette were: height 45 mm, width 12.5 mm, depth 12.5 mm, inner width 2 mm, volume 700 μl . The Raman characterization was carried out on a Bruker MultiRAM FT-Raman spectrometer using a diode-pumped Nd:YAG laser with a wavelength of 1064 nm and a liquid nitrogen cooled Ge diode detector. The laser power was set to 400 mW and data were collected in 5 min intervals. The spectra have been deconvoluted by fitting with three Voigt functions according to the experimental profile reported in the result and discussion part of the manuscript.

2.2. In-situ gel formation in the lithium cell

The membrane described previously (see Table 1) was prepared in-situ in a Swagelok, stainless steel electrode T-cell with geometric surface area of 0.785 cm^2 coupling lithium metal (Li-foil, 38 μm thick, Chemetall) and a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode prepared in our laboratory as reported in previous papers [8], using a glass fibre separator (type/A, Whatman®) to avoid short circuit, and a lithium metal anode. The in-situ gelification was performed by introducing the polymer solution (EC:DMC 1:1/PVdF, 80/20 wt) heated at 70 °C into the cell held at the same temperature, followed by a quench to room temperature. Subsequently, the LiPF_6 infiltration was



Scheme 1. Schematic representation of the in situ EC–DMC–PVdF gel formation (A) and LiPF_6 salt infiltration in the gel membrane (B).

performed by direct contacting the in-situ formed gel with LP30 (i.e., EC:DMC 1:1, LiPF₆ 1 M) for 300 min. The LP30 solution was added in a 2:1 v:v ratio, in order to get a final concentration of the salt in the gel electrolyte approaching 0.5 M, and completely removed from the cell after 3 h, after completion of LiPF₆ salt infiltration (see Scheme 1). The use of the LiPF₆ was avoided during the gelation procedure, this in order to prevent eventual reactions with the solvents upon heating.

Relevant DMC evaporation was not observed during the gel preparation, since the liquid precursors have been heated in a sealed bottle. However, a minor evaporation during the fast insertion of the liquid precursors into the cell before sealing, cooling and consequent gelation cannot be excluded.

The cell was galvanostatically cycled at room temperature using a C/5 rate (of about 0.15 mA cm⁻², with 1C current being 148 mA g⁻¹ with respect to LiNi_{0.5}Mn_{1.5}O₄ active mass having a loading of about 5 mg cm⁻²), within the voltage range 3.5–5.0 V employing a Maccor Series 4000 Battery Test System. The performance of the cell was evaluated in terms of specific capacity and cycle life.

3. Results and discussion

The procedure here reported for the gel-type electrolyte in-situ preparation involved two different steps: the gel membrane

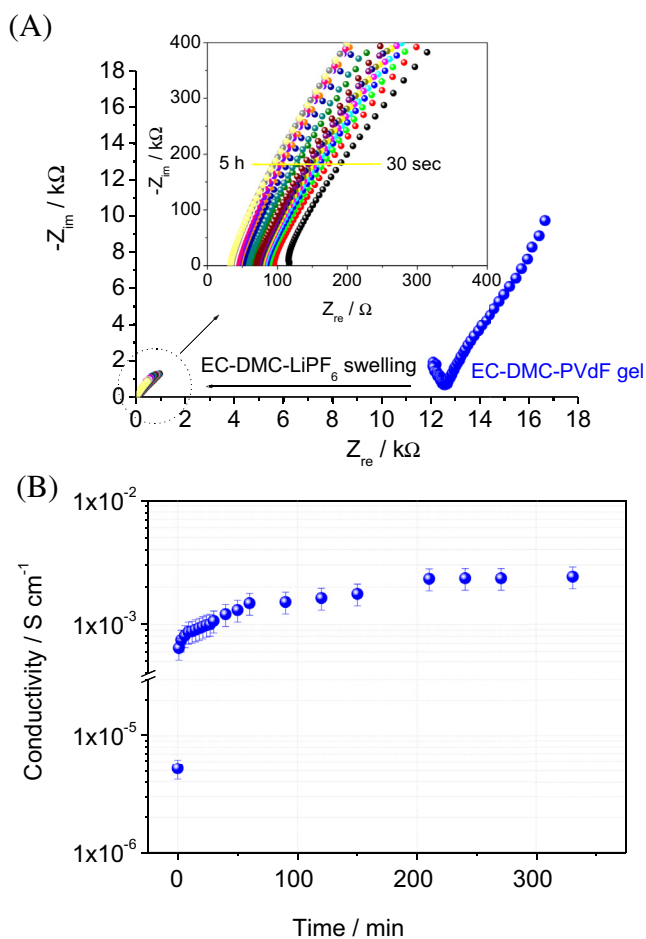


Fig. 1. Time evolution of the Nyquist impedance plots (A) and of the corresponding conductivity values (B) during PVdF-based gel infiltration by the LiPF₆ salt dissolved in a EC:DMC 1:1 solvent. 100 kHz–100 Hz frequency range, r.t.

formation and the lithium salt, i.e. LiPF₆, infiltration. The two-step procedure has been designed in order to avoid side reactions of LiPF₆ with the solvent, or the other cell materials, during the gel preparation, in particular considering that the process involves heating. In fact, fluorinated radicals may be generated by heating solutions containing LiPF₆ salt that may react with the hydrocarbons, this producing several fluorinated species, among them the HF, i.e. “very reactive specie” leading to severe cell degradation.

Prior to in-situ formation and use of the gel electrolyte in the lithium cell, we studied the behaviour of the membrane in terms of LiPF₆ salt infiltration “see also Experimental section”. Fig. 1 reports the Nyquist impedance plots (A) and the corresponding time evolution of the conductivity (B) during infiltration, clearly showing an initial, fast increase of the electrolyte conductivity from a value of about 4×10^{-6} S cm⁻¹– 4×10^{-4} S cm⁻¹ in the first few minutes, followed by a slower increase and stabilization to a value of about 3×10^{-3} S cm⁻¹. This behaviour proves that the lithium salt diffusion into the polymer matrix is fast.

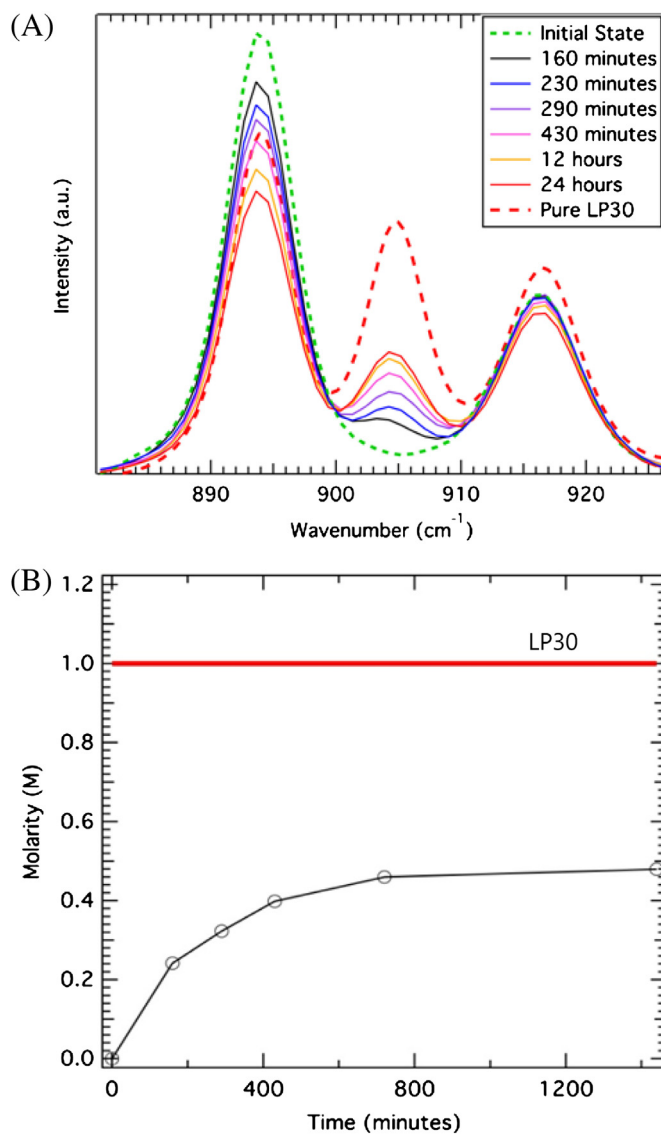
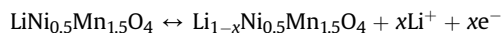


Fig. 2. Time evolution of the FT-Raman spectra (A) and corresponding variation of the diffused salt amount (B) during PVdF-based gel infiltration by the LiPF₆ dissolved in a EC:DMC 1:1 solvent at r.t. The molar concentration vs. time graph (B) was obtained by integrating the 905 cm⁻¹ band.

Similar behaviour is observed by the FT-Raman analysis reported in Fig. 2. The spectral range of 880–930 cm^{-1} had previously been used to study the solvation of Li by EC molecules (905 cm^{-1}) as a function of Lithium salt concentration [9]. A similar feature can be found for the DMC molecules at slightly higher wave numbers (about 934 cm^{-1}), which was however neglected for the calculation due to its low intensity and short acquisition times. Furthermore, the absence of Raman active modes of the PVdF within the studied range excluded eventual background subtraction. Two characteristic peaks, at 894 and 917 cm^{-1} corresponding to the ring breathing mode of EC [10] and to the C–O stretching mode of DMC [11], respectively, are observed for the gel-cast sample in its pristine state. As the Lithium salt diffuses into the gel-cast membrane, the characteristic feature of EC solvating Li-ions at 905 cm^{-1} appears [12] and its intensity increases upon time, as can be seen from the Raman spectra in Fig. 2A. The integrated area of this peak (see Experimental section) can be directly related to the lithium concentration (molar) in the gel membranes (Fig. 2B), which follows a similar trend to that observed in the conductivity plot, see Fig. 1B. For comparison, Fig. 2A reports the spectrum of the neat liquid electrolyte EC:DMC, LiPF₆ (LP30). One should notice that the liquid component in the final gel polymer electrolyte has a lithium salt concentration of the order of half of that of LP30. This is also reflected in an expected lower ionic conductivity, i.e. of the order of $3 \times 10^{-3} \text{ S cm}^{-1}$ vs. $1 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature, respectively, that is still well within the lithium battery application requirements [13].

Fig. 3 shows the voltage profile (A) and the cycling behaviour (B) of the lithium cell using a high voltage LiNi_{0.5}Mn_{1.5}O₄ spinel

cathode having a theoretical capacity of 148 mAh g^{-1} and the in-situ prepared polymer gel-type electrolyte, with the expected voltage signature of the LiNi_{0.5}Mn_{1.5}O₄ cathode [14] characterized by the following reaction mechanism:



The cell displays a reversible capacity of 120 mAh g^{-1} , with relatively low efficiency, i.e. of the order of 85%, during the initial 10 cycles. This is most likely due to SEI film formation at the electrode surface [15] with electrolyte decomposition at the high voltage of 5 V at the cathode side and structural readjustment upon initial lithium uptake/removal, typical of lithium-ion electrochemical processes [16]. During the following cycles the stabilization of the SEI layer prevents further decomposition and the cell efficiency values increases to about 97%, with remarkable reversibility during operation and high capacity retention. This demonstrated the applicability of the in-situ gelification method reported in this work.

4. Conclusion

In this paper we reported on an alternative approach for preparation of a Li-battery cell with the in-situ formation of a gel-type electrolyte as an innovative step. The electrolyte, characterized by electrochemical techniques and Raman spectroscopy, demonstrates an appropriate behaviour in terms of ionic conductivity and cell performance in a lithium battery using a high voltage spinel-type cathode. We believe that the approach adopted in this work may be successfully applied in lithium batteries, and that, upon proper optimization in terms of liquid-salt-polymer relative amount, the in-situ gelification can be proposed for a larger-scale process, in particular if recycling conditions are adopted. Further attempts, aimed at a full understanding of the physical phenomena involved in the in-situ gelation process here described will be reported in future papers, together with the electrochemical characterization of different Li-ion cell configurations adopting in-situ gelled polymer electrolytes.

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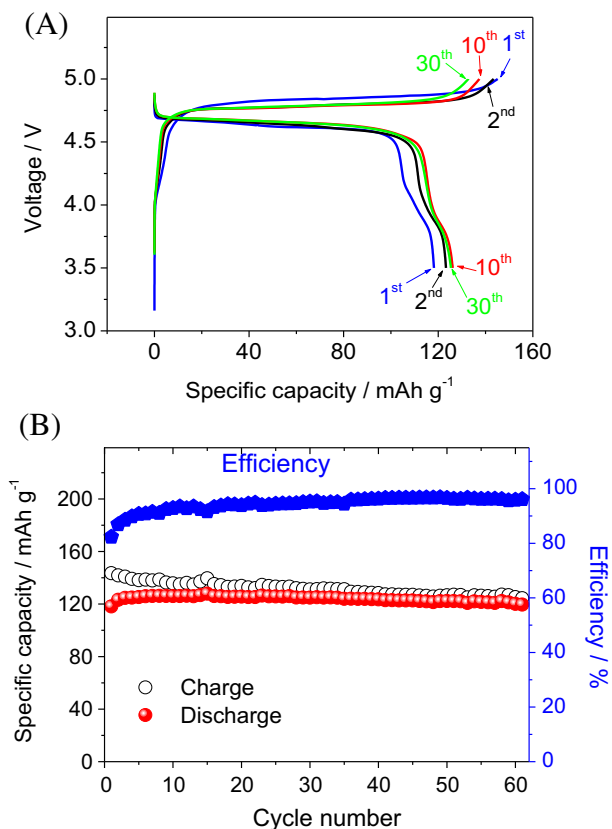


Fig. 3. Voltage profile (A) and the cycling behaviour (B) of the Li/PVdF-EC:DMC-LiPF₆/LiNi_{0.5}Mn_{1.5}O₄ cell in which the gel-type electrolyte was prepared in-situ as described in the paper.