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Evaluation of GPE performances in lithium metal battery technology by means of simple polarization tests

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Abstract

Gel polymer electrolyte (GPE) membranes based on two polymers, a copolymer of poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP), and the poly(ethylene oxide) (PEO), together with a plasticizer, the dibutylphtalate (DBP), were elaborated in two ways. Firstly, the polymers and the plasticizer were mixed together to obtain a single membrane. Secondly, a bi-layer separator membrane was made by adjunction, through lamination, of a DBP plasticized PVdF–HFP film and a homemade DBP–PEO thin film. We report here a protocol based on a simple galvanostatic polarization of Li/GPE/Li symmetric cells as a way to rapidly screen new viable membranes. Such a procedure enables to quickly discriminate separators by leading experiments that do no not exceed 1 week compared to hundreds of days needed with classical batteries. The validity of such an approach was confirmed by investigating the performances of the membranes in Li/GPE/$Li_4Ti_5O_{12}$ flat battery configuration. Besides, through this study we also highlighted the role of the macroscopic PEO–PVdF interface toward dendrite of bi-layered separator, while a single blended membrane does not seem to be suitable for a practical use. Post-mortem pictures and SEM investigation have confirmed this result.

Keywords: Gel polymer electrolyte; Lithium cells; Dendrites; Bi-layer separator; Blended membrane

1. Introduction

The continuous increase in the portable device market, such as mobile phones, laptop computers, has lead to the search for new electrochemical systems enabling to safely deliver sufficient power for a long time. For reasons of toxicity, Ni–Cd batteries are no longer a contestant in the race to equip the devices of this century. Actually, among the emerging technology (Ni–MH; Li–ion) the Li–ion batteries are at the moment the most efficient systems to supply the required power and energy. Nevertheless, the use of graphite-based composite electrode ($372\,mAh\,g^{-1}$) limits the expansion of their capacity needed in a near future. In order to replace graphite, lithium metal electrode ($3860\,mAh\,g^{-1}$) has long been identified as a promising alternative, but the interest rapidly declined due to the possibility of short-circuit associated to the lithium dendritic growth at the lithium metal surface upon cycling [1]. To circumvent this issue, Armand et al. suggested the use of a dry solid polymer electrolyte consisting of poly(ethylene oxide) (PEO) and a lithium salt [2]. While efficient, considering its ability to lower the dendritic growth, this type of separator operates well only above the polymer melting temperature, typically $T = 90\,^{\circ}C$. One of the most promising technologies for a room temperature application seems to be the use of gel polymer electrolyte (GPE) [3]. Our group recently investigated two different GPE configurations [4]. A classical approach consists in blending two polymers in order to obtain a unique membrane [5]. This separator, denoted hereafter blended membrane (BM), is composed of PEO domains swollen by the liquid electrolyte and a poly(vinylidene fluorine-*co*-hexafluoropropylene) (PVdF–HFP) framework, which brings the mechanical strength. On the other hand, a separator consisting of the adjunction of two films, one based on PVdF–HFP and the other based on PEO, was realized. This separator is denoted hereafter bi-layer separator (BLS). In this case, once swollen by the liquid electrolyte the PEO film enables the realization of a good interface

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with the lithium, while the PVdF–HFP film is used as an electrolyte sponge. The physico-chemical properties of both GPE have previously been investigated and reported [4]. Whatever the binary electrolyte used, the fundamental technical and scientific question of the dendritic growth remains. The aim of this paper is to propose a way to quickly and easily evaluate the ability of a given electrolyte to prevent short-circuits. To reach this goal, quick galvanostatic polarization experiments on Li/GPE/Li symmetric cells, and long galvanostatic cycling experiments on real battery configuration were performed and compared. Postmortem investigations have enabled us to validate our procedure and to propose a sketch of the dendritic growth in both studied GPE membranes.

2. Experimental

2.1. Membranes preparation

The blended membranes were prepared by gelling PVdF–HFP (Elf-Atochem, Kynarflex 2801 containing 12% of hexafluoropropylene units with $M_v = 3 \times 10^5$ g mol^{-1}) in highly purified acetone. PEO ($M_v = 4 \times 10^5$ g mol^{-1} from Aldrich) was solvated by acetonitrile. All products were used as received. Once homogeneous, the two gels were poured in a laboratory blender together with DBP (from Prolabo) according to the Bellcore process [6], and vigorously blended for 15 min. The optimal composition was previously found as being 3/7/10 (w/w) of PEO/PVdF–HFP/DBP, respectively. After evaporation of the solvents we obtained freestanding films about 50 μm thick.

For the BLS separator, 35 μm PVdF–HFP, SiO_2 and DBP-based membranes were made according to the Bellcore process using a 3/2/4 (w/w), respectively. PEO thin films were obtained by first mixing in acetonitrile high molecular weight PEO ($M_v = 4 \times 10^6$ g mol^{-1} from Aldrich) and DBP in a 1:1 (w/w) and then by casting the solution on a Mylar® sheet using a doctor blade apparatus gapped at 0.15 mm. After room temperature solvent removal, a 10 μm thick film was obtained and laminated on one side of a Bellcore's PVdF–HFP separator [7].

2.2. Symmetric cells and batteries assembly

To evaluate the behavior of the BM or BLS membranes under galvanostatic polarization, symmetric Li/GPE/Li cells have been prepared. The membranes were washed with ether to remove the DBP, dried and put into an Argon filled glove box to be impregnated with a solution of ethylene carbonate–propylene carbonate mixture (EC/PC 1:1, w/w) containing 1 M dissolved lithium salt $LiN(CF_3SO_2)_2$ (Lithium bis(TriFluoromethaneSulphonyl)Imide commercially known as LiTFSI). The electrolyte membrane was sandwiched between two lithium foils laminated on a copper grid used as current collector. A homemade polypropylene mask having a 2 cm^2 circular opening in its center was used to fix the active lithium surface area. Afterwards, the cells were sealed in hermetic coffee bags, and taken out of the glove box. Schematic drawings of the symmetric cells are given in inserts of Fig. 1.

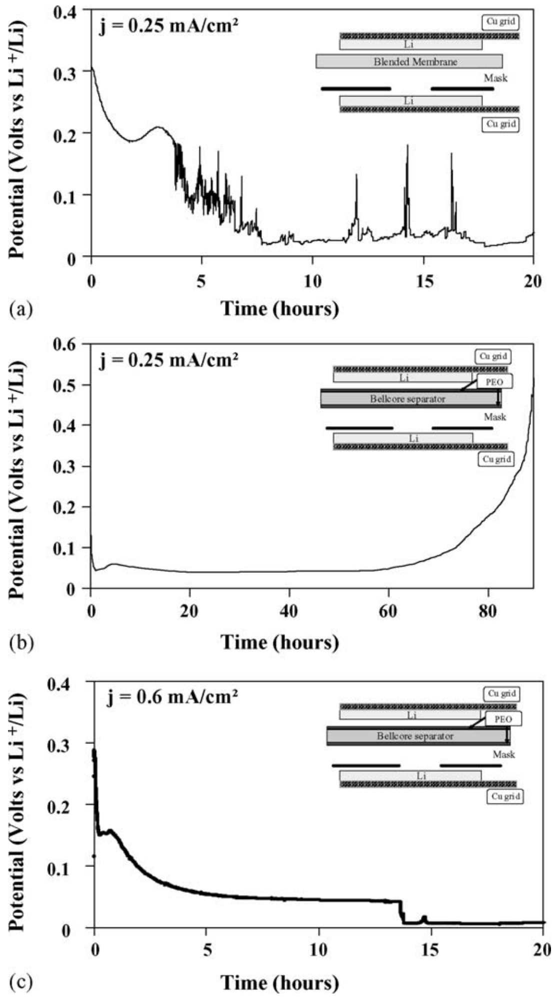

Fig. 1. Polarization curves of (a) a BM-based symmetric cells and (b) a BLS-based symmetric cell at $j = 0.25$ mA cm^{-2}. (c) Typical short-circuit observed on a BLS-based symmetric cell polarized at $j = 0.6$ mA cm^{-2}.

$Li_4Ti_5O_{12}$, provided by Telcordia technology, was used as a reference active material because of its high reversibility with regard to the lithium insertion/extraction [8]. Outside the glove box, 2 cm × 2 cm composite cathodes were prepared from a mixture of active material (56 wt.%), PVdF–HFP copolymer (15%), DBP (23%) and carbon black (6%) dissolved in acetone. The resulting slurry was spread onto a glass plate resulting in a 50 μm plastic film after solvent evaporation. Within these conditions, a $Li_4Ti_5O_{12}$ composite cathode having 3 mg of active material per square centimeter presents a capacity of about 0.5 mAh cm^{-2}. Cathodes were first laminated together with a pre-treated aluminum grid on one side. In the case of BLS-based batteries, a second lamination step was performed in order to stick the PVdF–HFP side of the membrane onto the positive electrode. Afterwards, once the DBP extracted by means of several washes into ether solutions, the half-cells were transferred into the glove box, where they were impregnated with liquid electrolyte. A lithium foil, pre-laminated on a copper grid, was then placed on top of the cathode/GPE half-cell to produce a battery. Finally, they were sealed in hermetic coffee bags, taken out of the glove