Short communication

Microporous gel electrolyte Li-ion battery

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Abstract

This paper describes the fabrication and performance of microporous gel electrolyte (MGE) Li-ion batteries. Fabrication of the MGE battery includes three steps: (1) making a microporous membrane separator by the phase inversion method, (2) activating the battery with a liquid electrolyte, and (3) forming MGE in situ by cycling the battery. The MGE contains three phases: liquid electrolyte, gel electrolyte, and a polymer matrix. MGE has advantages of high ionic conductivity, good adhesion to the electrodes, and good mechanical strength. In this work, poly(vinylidene fluoride-co-hexafluoropropylene) copolymer was used as the polymer matrix, and a solution of 1.0 m $LiBF_4$ dissolved in 1:3 (wt.) mixture of ethylene carbonate and γ-butyrolactone was used as liquid electrolyte. Typically, a MGE gelled with 120 wt.% of liquid electrolyte shows an ionic conductivity of 3.4 mS/cm at 20 °C and the resulting battery can withstand high temperature (60 °C) operation with low capacity fading.
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1. Introduction

Microporous polyolefin membranes have been widely used as a separator in Li-ion batteries. As a battery separator, polyolefin membranes have the disadvantages of: (1) poor wettability for many electrolyte solvents such as ethylene carbonate, propylene carbonate, and γ-butyrolactone, (2) poor ability in retaining liquid electrolyte, and (3) high interfacial resistance between the electrodes and separator. It has been reported that the Li-ion battery accumulates gaseous products after long-term operation [1]. These gaseous products are most probably trapped as bubbles between the electrodes and the separator, which significantly increases the internal resistance. Therefore, a method of bonding the electrodes and separator together was proposed to improve the contact of the electrodes and separator. To do this, a gel polymer electrolyte layer was coated on both sides of the porous polyolefin membrane or the surfaces of each electrode so that the gel polymer electrolyte not only serves as an adhesive but also provides an ionic conducting matrix [2,3]. However, this process is limited by many practical difficulties, such as: (1) the coating process must be conducted in an anhydrous environment due to the highly hydroscopic

property of the lithium salt and solvents, (2) the coating process may damage the electrode structure due to the solubility of the polymeric binder in the solvents used. Recently, Telcordia (formerly Bellcore) researchers developed an improved process, in which a plasticizer is first mixed into the polymeric layers to create the microporous structure and then a liquid electrolyte is introduced to gel the polymer [4]. This approach offers the advantage of allowing the battery to be fabricated in a non-anhydrous environment. However, it requires an additional procedure of extracting the plasticizer, which increases the cost of battery fabrication. On the other hand, the porous membrane method has been proposed to overcome difficulties of making the gel polymer electrolyte, in which a porous membrane is first prepared in a non-anhydrous environment and then activated with a liquid electrolyte [5–11]. In this method, the anhydrous operating environment is needed only in the last step of electrolyte activation.

With the above background in mind, we attempted to simplify the process of battery fabrication by designing a microporous gel electrolyte (MGE) Li-ion battery, in which the MGE comprises three phases: liquid electrolyte, gel electrolyte, and polymer matrix. Such a MGE can be made by using a swellable microporous separator, which is subsequently gelled with a liquid electrolyte. We speculate that the MGE can combine the advantages of the liquid electrolyte (high conductivity) and gel electrolyte (good adhesion to the

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electrodes). In this paper, we will present and discuss results of the MGE conductivity and the battery performance.

2. Experimental

Kynar Flex^{TM} 2801, a poly(vinylidene fluoride-co-hexafluoropropylene) copolymer from Elf Atochem North America, was used as a polymeric matrix of the MGE. The microporous membrane was prepared by the phase inversion method as follows: Kynar powder was dissolved into dried acetonitrile to obtain a 20 wt.% solution by stirring and heating at 60 °C. The warm solution was cast onto a Teflon-coated substrate using a doctor blade with a gap of 0.24 mm. The resulting dope was immediately immersed into a coagulation bath filled with deionized water to precipitate polymer. Due to fast exchange between the solvent and coagulation medium, a microporous membrane was formed in seconds and peeled off the substrate. This membrane was dried at 90 °C under vacuum for 16 h and cut into small discs of 2.85 cm^2 (diameter = 0.75 in.) for future characterization and use. The dried membrane has a white color due to its porous structure.

A solution of 1.0 m LiBF$_4$ dissolved in 1:3 (wt.) mixture of ethylene carbonate (EC) and γ-butyrolactone (GBL) was used as the liquid electrolyte. The MGE was prepared by dipping the microporous membrane into the liquid electrolyte for 1 day although the liquid electrolyte rapidly penetrated into the porous membrane to form a transparent film. After swelling, the excess liquid electrolyte on the surface was removed by pressing lightly between two sheets of filter paper. Generally, the porous membrane could absorb 120 ± 5 wt.% of liquid electrolyte compared with the weight of the dried membrane and the swollen membrane has a thickness of 0.14 mm. To measure ionic conductivity, the swollen membrane was sandwiched between two stainless steel plates and sealed in a 2325-type button cell. The conductivity was calculated from the impedance of the cell.

Standard electrodes from SAFT America, Inc. were used to evaluate the cycling performance of the MGE Li-ion battery. The cathode active material was a lithiated nickel based mixed oxide and the anode was graphite. The cathode and anode were dried at 110 °C under vacuum for 16 h and cut into discs of 0.97 and 1.27 cm^2, respectively. Cell stacks consisting of anode, porous membrane, and cathode were assembled and activated with 150 μm of liquid electrolyte. After being sealed, the cells were heated at 80 °C for 10 min to promote formation of the MGE. Then, the cells were charged to 4.2 V at a slow current rate of 0.1 mA/cm^2, followed by cycling twice between 2.5 and 4.2 V at the same current to complete formation of the solid electrolyte interface (SEI).

A Tenney Environmental Oven Series 942 was used to control the temperature of the cells. Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer were employed to measure impedance. For conductivity, the impedance was measured over the frequency from 100 kHz to 1 Hz with an ac oscillation of 10 mV. For the Li-ion cell, the impedance was measured potentiostatically by applying a dc bias and an ac oscillation of 10 mV over the frequency range from 100 kHz to 0.01 Hz. The voltage, at which the impedance was measured, was achieved by galvanostatically cycling the cell at a current density of 0.1 mA/cm^2. The obtained impedance spectra were analyzed using ZView software. A Maccor Series 4000 tester was used to cycle the cells. In cycling tests, the cell was charged at 0.5 mA/cm^2 to 4.1 V and then kept at 4.1 V until the current to 0.05 mA/cm^2, followed by discharging at 0.5 mA/cm^2 to 2.5 V.

## 3. Results and discussion

3.1. Preparation and morphology of microporous membrane

Phase inversion has been a well-known technology for making microporous polymer membranes [12–15]. Formation of the porous structure is based on the exchange between solvent and non-solvent, or called coagulation medium, in the polymer solution. Therefore, the properties of the two solvents significantly affect the morphology and porosity of the resulting membrane. In this work, we chose acetonitrile as a solvent and water as a non-solvent because (1) there is excellent miscibility between these two solvents and (2) acetonitrile has a lower boiling point than that of water. The excellent miscibility ensures a rapid exchange of the solvents, and the lower boiling point of the solvent can reduce the collapse of the formed pores in the case of the residual solvent due to prior evaporation of the solvent to the non-solvent. Therefore, the present choice of the solvent and non-solvent can greatly shorten the time of membrane fabrication, which is highly desirable in large-scale manufacturing.

It has been reported that the morphology of poly(vinylidene fluoride) based microporous membrane varies from "sponge-like" to "finger-like", depending on the solvent and non-solvent pair used [7,10,11,14,15]. The membrane made in this work has a "sponge-like" structure with asymmetric distribution of the pores on both sides of the membrane (Fig. 1). The size of the pores on the top side is not larger than 1.5 μm in diameter, while that on the bottom side is much smaller. The asymmetric structure is caused by different kinetics in the phase inversion between the two sides of the dope. On the bottom side, the exchange between the solvent and non-solvent is blocked by the substrate, which results in the less porous structure. In addition, the porosity of the membrane can be controlled by the concentration of the polymer solution, the gap of the doctor-blade, and the temperature of the coagulation bath. It was found that the membrane made under the conditions of the present work can absorb 120 ± 5 wt.% of liquid electrolyte compared to the weight of the dry membrane.
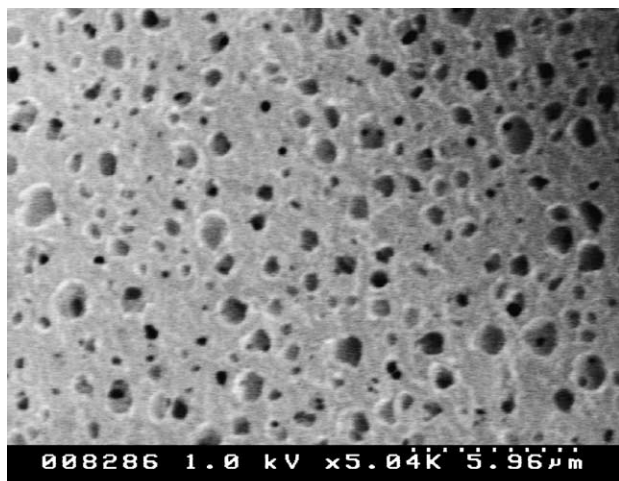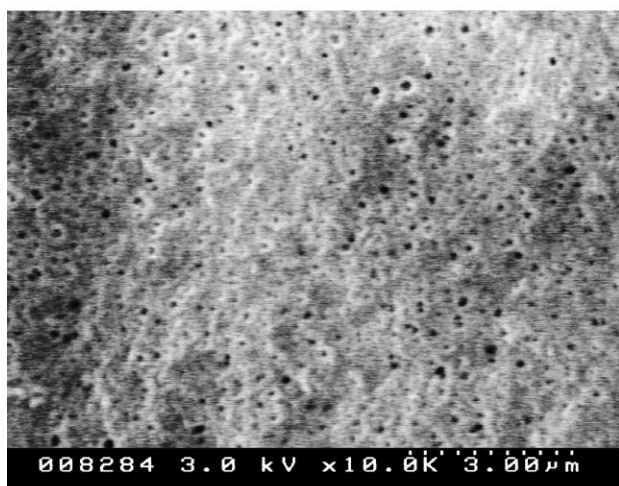
Fig. 1. SEM microphotos of the microporous membrane. (a) Top side, which faced to air during the phase inversion process; (b) bottom side, which contacted the substrate.

3.2. Structure and conductivity of MGE

The porous membrane itself can serve as a separator by trapping liquid electrolyte in its micro voids. However, the Kynar is swellable by many electrolyte solvents used in Li-ion batteries [16]. Therefore, a MGE can be formed when diffusion of the liquid electrolyte is restricted. In the MGE, three phases of liquid electrolyte, gel electrolyte, and polymer matrix are present, as illustrated in Fig. 2. It is obvious that the MGE combines the advantages of high conductivity (liquid), good adhesion (gel), and stable dimension (solid polymer matrix). Fig. 3 shows Arrhenius plots for the ionic conductivities of the MGE and liquid electrolyte. The continuous and curved profile of the Arrhenius plot suggests that the MEG undergoes no phase-transition (e.g. freezing of liquid electrolyte) even at $-50\,^{\circ}$C. This can be ascribed to (1) high solubility of $LiBF_4$ in GBL, (2) low melting point ($-45\,^{\circ}$C) of GBL, and (3) good miscibility between EC and GBL. MGE has an ionic conductivity of 3.4 mS/cm at 20 $^{\circ}$C, in comparison with 6.4 mS/cm for the liquid electrolyte. The high conductivity of the MGE is in part attributed to the presence of free liquid electrolyte in the pores of the membrane.

3.3. Assembly of MGE Li-ion battery

In a practical fabrication, the MGE can be formed in situ after assembly of the Li-ion battery. As usual, the Kynar microporous membrane is used as a separator to assemble a liquid electrolyte battery. Initially, the liquid electrolyte is spread throughout the electrodes and the membrane. Due to the presence of liquid electrolyte, the fresh battery can be immediately cycled, during which the polymer (Kynar) is gradually swollen to form MGE. The advantage of the above process is that it leaves the electrolyte activation until the cell is finally sealed. In addition, the resulting gel electrolyte tightly bonds the electrodes and MGE separator together, which greatly reduces interfacial resistance.

Fig. 4 shows the voltage–capacity curve of the first 2 cycles of a MGE Li-ion cell. The coulomb efficiency of the first 2 cycles is calculated to be 83.8 and 99.0%, respectively. During these 2 cycles, not only is the formation of SEI completed, but the MGE structure is also formed. To confirm the MGE structure, the impedances of the resulting Li-ion cell at various state-of-charge (SOC) were measured and shown in Fig. 5. It is shown that the impedance spectra are composed of three overlapped semicircles and a straight line at the low frequency end. For a liquid electrolyte cell, such a pattern (three semicircles) can be observed only at low temperatures, where multi conducting phases may be present [17]. In the present case, the semicircle at the highest frequency region can be ascribed to multi conducting phases of the MGE, as discussed above. A similar conclusion has also resulted from the NMR analysis, which revealed that two conducting phases of liquid electrolyte and gel electrolyte exist in the MGE [8,9,11]. The other two semicircles of the impedance spectra in the medium and low frequency regions can be assigned to the SEI layer and charge-transfer process. It can be seen in Fig. 5 that the resistances of the MGE and SEI are independent of the SOC, while that of the charge-transfer process changes significantly with the SOC. In most of the SOCs, the charge-transfer resistance dominates the impedance of the whole the battery, which is the same case as for liquid electrolyte batteries. Therefore, we may conclude that the conductivity of the MGE would not be the main limitation in the cycling performance of the MGE Li-ion battery.

3.4. Cycling performance of MGE Li-ion cell

Fig. 6 compares the cycling performance of two MGE Li-ion cells, which were run at room temperature and at 60 $^{\circ}$C, respectively. It is shown that at 60 $^{\circ}$C the MGE cell retained almost the same capacity as at room temperature.
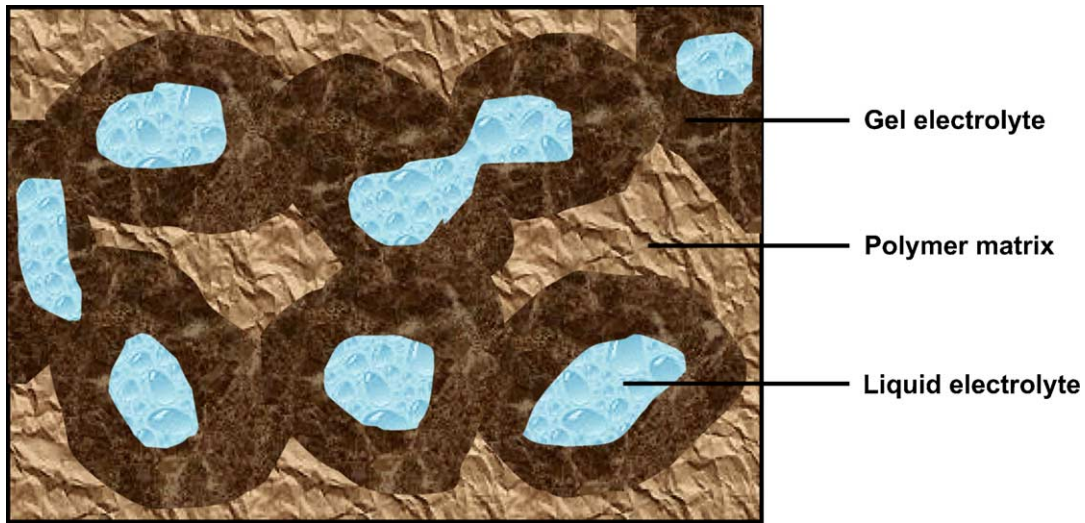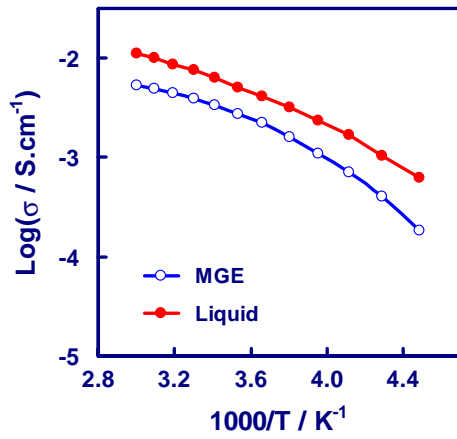
Fig. 2. A model of the MGE structure.

Fig. 3. Arrhenius plots of the ionic conductivities of the MGE and liquid electrolyte.

This fact verifies that the MGE separator can withstand 60 °C without significant loss in mechanical strength. Such a feature is one of the most important merits of the MGE, as compared with the conventional gel polymer electrolyte.
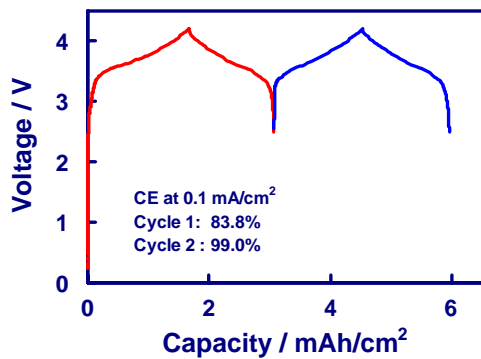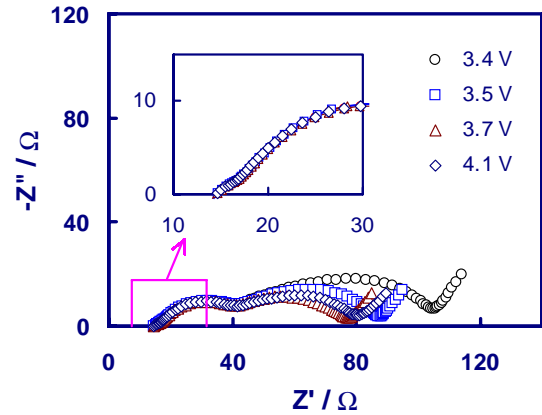

Fig. 5. Impedance spectra of the MGE Li-ion cell at various state-of-charge, which was recorded at 20 °C.

At elevated temperature, the gel polymer electrolyte usually becomes too fluid to serve as a separator unless some inorganic fillers such as silica and alumina are hybridized to strengthen its structure [18].

Fig. 4. Voltage–capacity curve of the first 2 cycles of the MGE Li-ion cell, which was recorded at 0.1 mA/cm².
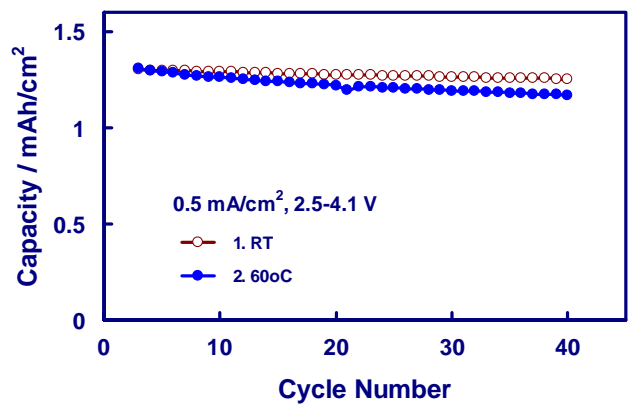

Fig. 6. Comparison of cycling performance of the MGE Li-ion cell at room temperature and 60 °C.
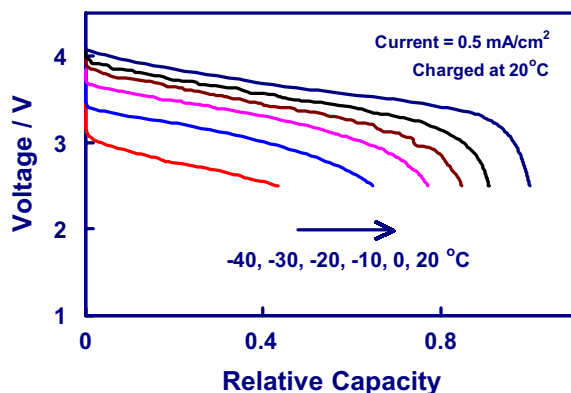
Fig. 7. Low temperature performance of the MGE Li-ion cell, which was recorded by charging the cell at 20 °C and discharging at a specific temperature.

Fig. 7 shows discharge curves of the MGE cell at low temperatures. In this experiment, the cell was charged at 20 °C and discharged at a specific temperature. To describe capacity retention at various temperatures, we used a term of "relative capacity", which was defined as the ratio of the capacity at a specific temperature to that obtained at 20 °C. It is shown that the MGE cell retained as high as 0.65 of the relative capacity even at-30 °C. In our early work [19,20], we found that the LiBF$_4$ salt can greatly reduce the charge-transfer resistance of the battery reactions and that the extremely high charge-transfer resistance is the main limitation to the low temperature performance of the Li-ion battery. Therefore, the excellent low temperature performance, as shown in Fig. 7, can be attributed to the use of LiBF$_4$ salt.

Fig. 8 compares discharge curves of the MGE cell at various current densities. For a fair comparison, the same charging conditions were applied to all cycles. The cell was charged to 4.1 V at 0.5 mA and then kept at 4.1 V until the current density dropped to 0.05 mA. It can be seen that even at the current rate of 4 mA (~3.1 C), the cell retained 84% of capacity with little loss in the power (operating voltage), as compared to that obtained at 0.5 mA. This good rate
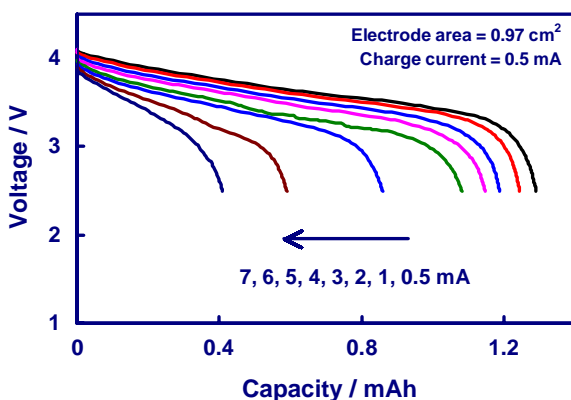
performance can be ascribed to the high ionic conductivity of the MGE and to the low interfacial contact resistance between the electrodes and MGE due to use of the highly adhesive MGE. The results of Figs. 6–8 have indicated that the MGE Li-ion battery can be operated in wide temperature range and at high current rate.

4. Conclusions

The present work shows that the MGE battery can be fabricated by in situ gelling of a pre-prepared microporous separator. Due to the fact that the separator is porous and the polymer matrix is swellable, three phases of liquid electrolyte, gel electrolyte, and polymer matrix may be present in the MGE. Therefore, the MGE can combine the advantages of the liquid electrolyte (high conductivity), gel electrolyte (low interfacial resistance between electrodes and electrolyte), and solid electrolyte (stable dimension over a wide temperature range). It was found that the MGE could withstand high temperature (60 °C) operation without degradation function.

Fig. 8. Comparison of discharge capacities of the MGE Li-ion cell at various current densities.

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