Short communication

Submicroporous/microporous and compatible/incompatible multi-functional dual-layer polymer electrolytes and their interfacial characteristics with lithium metal anode

Young-Gi Lee [a],*, Kwangseuk Kyhm [b], Nam-Soon Choi [c], Kwang Sun Ryu [a]

[a] *Ionics Devices Team, Electronics and Telecommunications Research Institute, 161 Gajeong-dong, Yuseong-gu,
Daejon, 305-700 Daejeon, Republic of Korea*
[b] *Research Center for Dielectric and Advanced Matter Physics, School of Physics, Pusan National University,
San30 Jangjun-dong, Kumjung-gu, 609-735 Pusan, Republic of Korea*
[c] *Energy Lab., Samsung SDI Co. Ltd., 428-5 Gongse-ri, Giheung-eup, 449-577 Yongin, Republic of Korea*

Abstract

A novel multi-functional dual-layer polymer electrolyte was prepared by impregnating the interconnected pores with an ethylene carbonate (EC)/dimethyl carbonate (DMC)/lithium hexafluorophosphate ($LiPF_6$) solution. An incompatible layer is based on a microporous polyethylene (PE) and a compatible layer, based on a poly(vinylidenefluoride-co-hexafluoropropylene) (P(VdF-co-HFP)) is sub-microporous and compatible with an electrolyte solution. The Li electrode/the dual-layer polymer electrolyte/Li[$Ni_{0.15}Li_{0.23}Mn_{0.62}$]$O_2$ cell showed stable cycle performance under prolonged cycle number. This behavior is due to the enhanced compatibility between the matrix polymer and the liquid electrolytes within the submicroporous compatible layer, which could lead to a controlled Li^+ deposition on the Li anode surface by forming homegeneous electrolyte zone near the anode.

Keywords: Dual-layer; Polymer electrolyte; Compatible layer; Li^+ deposition; Cycle life; Homogeneous electrolyte zone

1. Introduction

Although theoretically the most promising, lithium metal polymer battery (LMPB) have encountered difficulties for commercialization because of poor safety and cycle performance. These problems are associated with the reactivity of Li anodes, the growth of dendrites, and dead Li formation at the anode surface upon cycling [1,2].

Penetration-growth of dendrite through a electrolyte film is mainly responsible for the short-circuit during the charging stage, and Li^0 powders stripped from the dendritic anode surface into the electrolyte solution during the discharging stage can lead to an explosion or fire when exposed to humid conditions. On repeated charge and discharge cycles, as lithium dendrites gradually grow out from the lithium metal anode surface, thickness of anode and total volume of cell increase, which result in reduced volumetric energy density and cycle life. Thus, the uniform Li^+-plating issue on the Li anode surface during the charging process is the key point to overcome these problems.

For past two decades, there have been various attempts to improve the safety and cycle life of LMPB by developing manifold solvent-free and plasticized polymer electrolytes [3–7]. However, they still have performance limits such as a low ionic conductivity at the ambient temperature and poorer mechanical properties than separator/liquid electrolyte systems in lithium-ion battery (LIB).

We have introduced a novel multi-functional polymer electrolyte having a dual-layer film structure which comprises an incompatible porous polymer film with microscaled pores and excellent mechanical strength based on PE and a compatible porous polymer film with submicron-scaled pores and good compatibility with liquid electrolytes based on P(VdF-co-HFP), which is coated on a surface of the incompatible polymer film [8–10].

In this study, we tried to investigate the interfacial characteristics between Li anode and the dual-layer polymer electrolyte to explain the improved long-term stability of the Li/the dual-layer polymer electrolyte/Li[Ni$_{0.15}$Li$_{0.23}$Mn$_{0.62}$]O$_2$ cell over the reference cell using separator.

2. Experimental

2.1. Preparation of dual-layer polymer electrolytes

The appropriate amount of P(VdF-co-HFP) and silanized fumed silica (TS-530, CAB-O-SIL) were completely dissolved and dispersed in acetone after being homogenized for 24 h in a laboratory ball mill. The viscous compatible polymer solution was coated on one side of microporous PE incompatible membrane with a doctor. A dual-layer film structure is comprised of an initial porous polymer film which micron-scaled pores based on PE and a secondary porous polymer film with submicron-scaled pores based on P(VdF-co-HFP) coated on the surface of the first porous polymer film, both of which are shown in Fig. 1. Specially, silanized fumed silica was used to aid for generating submicroporous structure within P(VdF-co-HFP) matrix and to form a homogeneous electrolyte zone in the submicroporous compatible layer throughout enhancement in the uptake amount of the liquid electrolytes. The dual-layered films were impregnated with a liquid electrolyte solution (1 M LiPF$_6$ in EC/DMC (1/1, w/w)).

2.2. Preparation of unit cells

Impedance of the specimen was measured over the frequency range of 0.1 Hz to 1 MHz using the Solartron 1255 frequency response analyser (FRA). The cathode was prepared by coating the slurry of 80% Li[Ni$_{0.15}$Li$_{0.23}$Mn$_{0.62}$]O$_2$ powder synthesized by a simple combustion method, 12% super-P carbon, and 8% PVdF binder on aluminum foil. A unit cell (2 cm × 2 cm) was fabricated by sandwiching the dual-layer polymer electrolyte between a Li metal anode (250 μm thickness, Chemetall Foote Corp.) and the cathode. The charge/discharge cycling test of the cell was conducted galvanostatically using battery testing equipment (TOSCAT-3000U) between 4.7 and 3.0 V with a current density of 0.5 mA cm^{-2} (C/5 rate).

3. Results and discussion

3.1. Charge/discharge capacities of LMPB unit cell with cycle number

Fig. 2(b) shows the specific charge and discharge capacities of LMPB unit cell with repeated cycle number. The dual-layer polymer electrolyte used in the LMPB unit cell had been already optimized in our previous studies as 6 μm submicroporous, compatible layer and 16 μm microporous, incompatible separator. 40 wt.% silanized fumed silica was added to the 6 μm compatible layer [9,10]. A bare PE separator of 20 μm thickness was employed in the unit cell for comparison as shown in Fig. 2(a).

The fabricated unit cell using the dual-layer polymer electrolyte shows excellent rechargeability and stable cycle behavior. However, for the unit cell prepared with the PE separator, it shows low coulombic efficiency after 250 cycles and abrupt rise in charge capacities (open square) is also observed in some cycle steps. Such a significant abnormal increase of charge capacity is mainly associated with gradual leakage of current as the dendritic Li grows toward cathode penetrating through the electrolyte film, namely soft short-circuit. After then, when discharging process, the mossy Li dendrite could be easily taken away to form dead, powdery Li within the electrolyte region and might result in abrupt capacity loss and decease. With the dual-layer polymer electrolyte system, it does not show any serious abnormal increase of charge capacity and abrupt discharge capacity fade with the repeated cycle.

The specific discharge capacities (filled square) of the unit cells versus cycle number are also shown in Fig. 2. For the PE separator system, the initial discharge capacity of 232 mAh g^{-1}
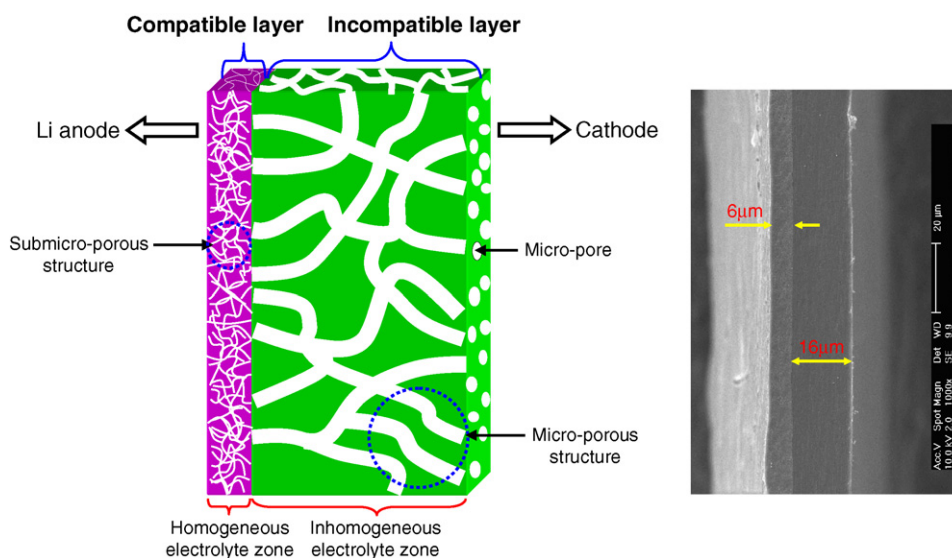

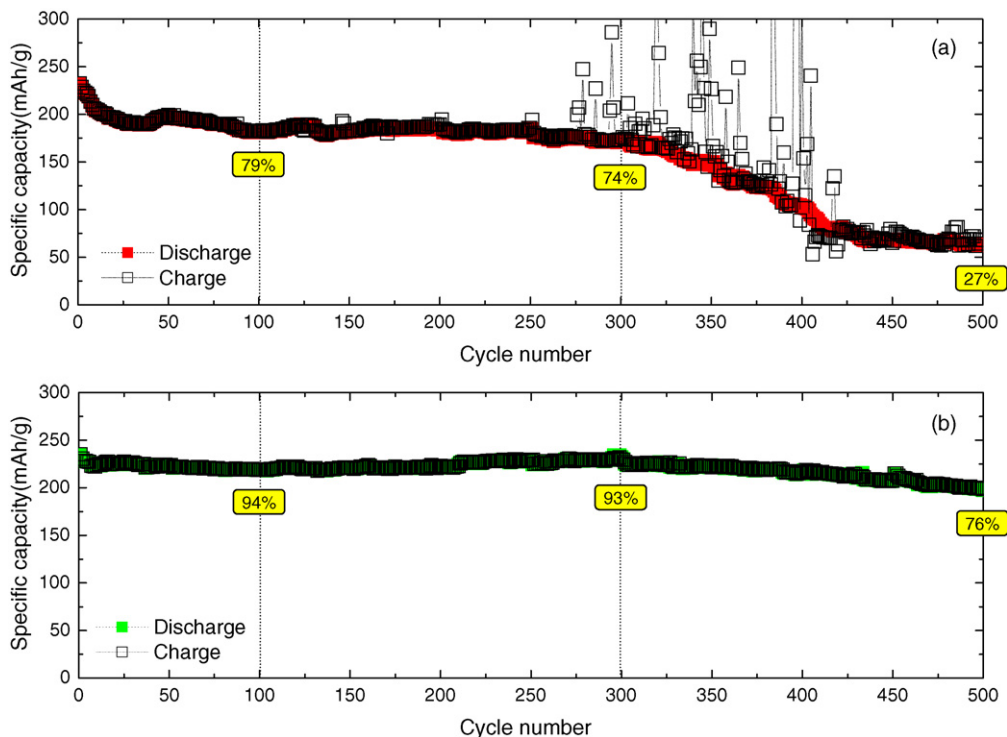Fig. 1. The schematic feature and cross-sectional SEM image of the dual-layer polymer electrolyte system.

Fig. 2. Charge and discharge capacities of the Li/the dual-layer polymer electrolytes/Li[Ni$_{0.15}$Li$_{0.23}$M$_{n0.62}$]O$_2$ cell with cycle at a constant current density of 0.5 mA cm^{-2} (2 cm × 2 cm, C/5 rate): the cell using (a) separator (Ref.) (b) dual-layer polymer electrolyte (6 μm coated).

falls to 183 mAh g^{-1} at 100 cycles, 172 mAh g^{-1} at 300 cycles, and 63 mAh g^{-1} at 500 cycles, as (a) in Fig. 2 shows. About 21% of its initial discharge capacity is lost during the first 100 cycles, and the remaining capacity is around 27% of its initial value after 500 cycles. This capacity fade also could be associated with the interfacial characteristics between the Li anode and the electrolyte film. Since the PE separator is not compatible with the liquid electrolyte, the gradual leakage of liquid electrolyte from the PE matrix during the cycles would accelerate the dendrite formation and growth to give a large reactive surface area, which leads to an SEI formation on the dendritic anode surface. The formation of voids or the delamination at the interface may reduce the effective contact area between the Li anode and the electrolyte film [7,9,11].

However, with the introduction of the compatible, submicroporous layer on the separator film, the capacity fade could

be reduced and show more stable cycling behavior. The initial capacity becomes 97% at 300 cycles and 87% of the initial value at 500 cycles, which indicates the significant improvement in cycling performance of the LMPB unit cell. This enhancement may be due to the Li$^+$-plating site control during the charging stage by forming a homogeneous electrolyte zone.

3.2. Interfacial characteristics of Li anode/dual-layer polymer electrolyte interface with cycle number

For the investigation of the stability of the Li interface in electrolyte cells, impedance spectroscopy was used. Accordingly, evaluation of the interfacial characteristics has been carried out by monitoring ac impedances of the unit cells in every 50 cycles. Fig. 3(a) represents the evolution of electrolyte resistances (R_b) for the unit cells. The PE separator system shows much larger
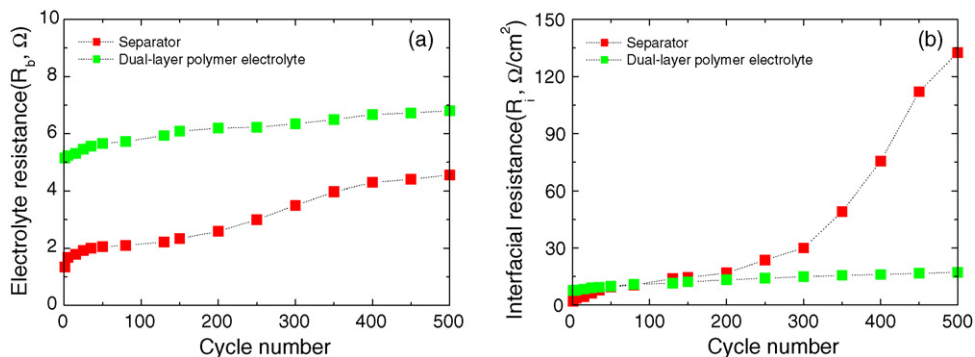

Fig. 3. Resistances of the unit cell with cycle: (a) electrolyte resistances (R_b) of the unit cell and (b) interfacial resistances (R_i) of the unit cell.
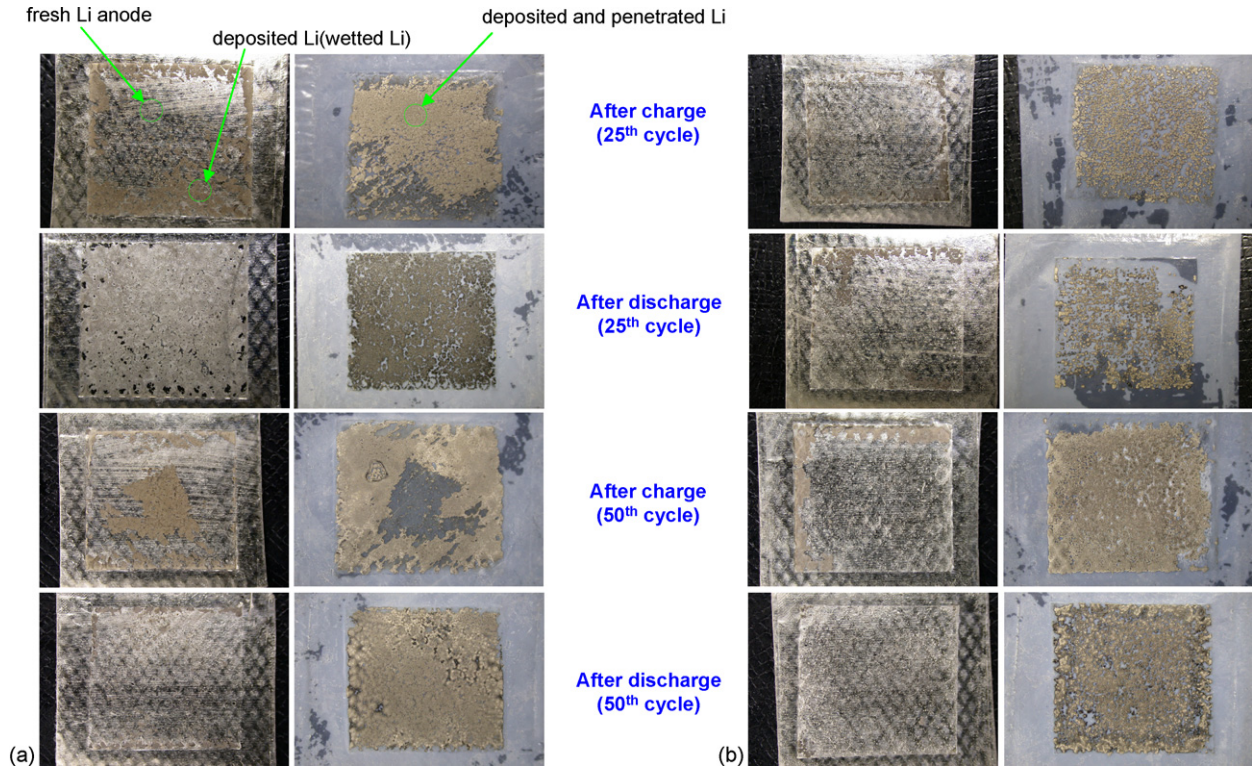
Fig. 4. Optical micrographs of the detached electrolyte film and Li anode surfaces from the unit cells at 25th and 50th cycle: (a) detached Li anode and the separator and (b) detached Li anode and the dual-layer polymer electrolyte (6 μm coated).

increase in the R_b during the cycle than the dual-layer polymer electrolyte based unit cell. This result demonstrates its evidence for the gradual leakage of liquid electrolyte from the PE matrix during the cycles due to the poor compatibility between the matrix polymer and the liquid electrolytes. Thus, this may indicate that the nature of the Li passivation process or Li dendrite formation at the Li interface could be progressively influenced by leaked liquid electrolytes.

Fig. 3(b) illustrates the evolution of interfacial resistances (R_i) of the unit cells with cycle number. The dual-layer polymer electrolytes based unit cell shows almost constant R_i values. The different behavior in the interfacial stability between the polymer electrolyte and the PE separator would be associated with the difference in the growth behavior or structure of the passive layer (SEI layer) and Li dendrites formed between the Li electrode and the electrolyte films. The leakage of liquid electrolytes would significantly influence the formation of the rough and mossy surface morphology of the Li anode.

Fig. 4(a) shows the optical micrographs of detached Li anode and PE separator surfaces at 25th and 50th cycle, respectively. A number of Li dendrite on the anode surface seems to be formed and penetrate toward the separator. We can observe that a lot of penetrated Li dendrite are stuck in the matrix polymer and even worse at 50th cycle. However, in the case of the dual-layer polymer electrolyte system, much less distribution of dendrite stuck was found on the surface of the electrolyte film at 25th and 50th cycle, as shown in Fig. 4(b). From the SEM images (1000×) of the Li anode surface in the unit cells after 500 cycles, we could also confirm that the PE separator system, as shown in Fig. 5(a), illustrates very rugged and seriously dendritic
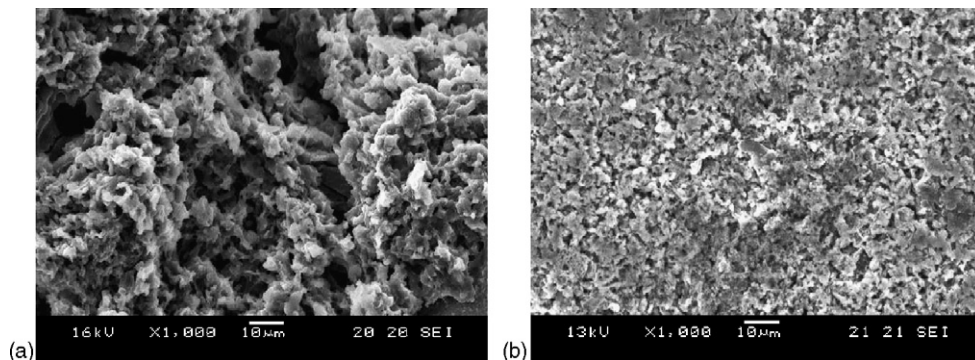

Fig. 5. SEM images (1000×) of the Li anode surfaces of the unit cells after 500 cycles: the cell using (a) separator (Ref.) (b) the dual-layer polymer electrolyte (6 μm coated).

surface morphology than the dual-layer polymer electrolyte (Fig. 5(b)).

4. Conclusion

This dual-layer type polymer electrolyte approach enabled a good cycling performance of LMPB unit cell to avoid severe dendrite formation and growth during the charging stages. The capacity loss was successfully reduced for the optimally fabricated unit cell. The increase in the interfacial stability seems to be associated with the compatibility of the matrix polymer with the liquid electrolyte.

Acknowledgements

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