Flexible, high-voltage and free-standing composite polymer electrolyte membrane based on triethylene glycol diacetate-2-propenoic acid butyl ester copolymer for lithium-ion batteries

QiuJun Wang^a, Wei-Li Song^a, Li-Zhen Fan^{a*} and Yu Song^{b*}

^a Institute of Advanced Materials and Technology, University of Science and Technology Beijing,
Beijing 100083, China

^b Shenzhen Key Lab of Electrochemical Storage Devices, Research Institute of Tsinghua University
in Shenzhen, Shenzhen 518057, China

*Corresponding author: Tel./fax: +86-10-62334311;

E-mail: fanlizhen@ustb.edu.cn; songyu@tsinghua-sz.org

Abstract

Composite polymer electrolytes (CPE) based on triethylene glycol diacetate-2-propenoic acid butyl ester (TEGDA-BA) incorporating Al₂O₃ nanoparticles have been fabricated via *in situ* polymerization. The CPE have exhibited highly uniform morphology, excellent mechanical property (maximum stress up to ~1.3 MPa), high ionic conductivity up to $3.92 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C, coupled with very high electrochemical stability (>5.0 V vs. Li/Li⁺). The Li|CPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cells have demonstrated remarkably stable charge/discharge performance and great capacity retention in the potential range of 2.0-4.8 V. The unexpected growth of interface resistance has been retarded with the presence of Al₂O₃, indicating the enhancement of the interface stability. The results suggest that the CPE have demonstrated tremendous application potential in high-voltage lithium ion batteries.

Keywords: Polymer electrolyte; alumina; composites; lithium ion batteries

1. Introduction

Rechargeable lithium-ion batteries (LIBs) with high energy are recommended as a promising power source [1, 2]. Compared to common liquid electrolytes [3], dry solid polymer electrolytes (SPE) generally offer low ionic conductivity although various attempts have been made, thus still suppressing their practical applications in LIBs [4-7]. As an alternative electrolyte, gel polymer electrolytes (GPE), formed by immersing a large amount of liquid organic electrolytes into polymer frameworks, have presented much enhanced ionic conductivities. However, their poor mechanical properties still limit their applications [8-11]. To address the problems, ceramic fillers such as SiO_2 [12-14], Al_2O_3 [15, 16], TiO_2 [17, 18] have been incorporated into polymer matrices to develop a new family of composite polymer electrolytes (CPE). It has been noticeable that the addition of ceramic fillers can offer improved ionic conductivity, safety, and in particular, electrolyte/electrode compatibility [19-21]. In the CPE, it is reported that the ceramic particles can promote electrochemical properties by acting as a source of charge carriers when the particle surface is appropriately modified [22, 23]. Also, densely packed Al_2O_3 nanoparticles have been added into polymer matrix to form a special CPE of unique microstructure, which demonstrates significant improvements in the mechanically compliant and lithium dendrite growth-suppressing [24]. In most current studies, the charge/discharge properties of LiCoO_2 , LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based electrodes have been reported. However, very little work has been done on the compatibility between CPE and high-voltage Li-excess nickel manganese oxide cathodes. Especially, the influences of different cut-off voltages and temperatures on cycling performance have rarely been investigated. Our previous study has reported cross-linked GPE composed of triethylene glycol diacetate (TEGDA)-2-propenoic acid butylester (BA) copolymer and liquid organic electrolytes via *in situ*

polymerization [25]. The liquid electrolyte is well dispersed in the polymer matrix, by which high ionic conductivity and electrochemical properties have been achieved. However, one of the shortages is the inadequate mechanical property caused by the fluidity of the solvents in GPE [26]. Thus, Celgard 2400 is still required to serve as the separator in the fabrication for cells. In current work, a new CPE with the addition of Al_2O_3 nanoparticles into the cross-linked TEGDA-BA has been fabricated. As functional fillers, Al_2O_3 nanoparticles are utilized to improve mechanical properties, interfacial stability of the electrodes, and cell safety. The cycling stabilities of the cells at different cut-off voltages and test temperatures, which are rarely investigated, have been discussed.

2. Experimental

In a typical preparation, Al_2O_3 (10~20 nm, Alfa Aesar), TEGDA ($\text{C}_{12}\text{H}_{18}\text{O}_6$), BA ($\text{C}_7\text{H}_{11}\text{O}_2$) and 2, 2'-Azobis-(2, 4-dimethylvaleronitrile) (ABVN, $\text{C}_{14}\text{H}_{24}\text{N}_4$) were mixed into 1 M LiPF_6 /ethylene carbonate (EC): dimethylcarbonate (DMC): ethylmethylcarbonate (EMC) (1:1:1 in volume) (CAPCHEM Co., LTD.) to form precursor solution by ultrasonic stirring for 4h. The composition ratio of precursor solution was (liquid electrolyte/monomer = 94/6 w/w)/ Al_2O_3 = 95/5 w/w, wherein concentration of TEGDA and BA was in a weight ratio of 4:2 and ABVN (thermal initiator) was 1 wt% of the monomer mixtures. Herein, the concentration of Al_2O_3 (5 wt%) is much lower than other CPE membranes (Al_2O_3 , ~300 nm, 70 wt%) in previous work [24]. Then, the precursor solution was cast onto a Teflon plate, followed by being sealed in a closed glass dish. Finally, the CPE were formed by heating the above mixture at 80 °C (30 min) for *in situ* thermal polymerization. For comparison, the CPE without Al_2O_3 were also prepared under the same conditions. All the procedures were carried out in the glove box under argon atmosphere (H_2O <1ppm).

The surface morphology was characterized by a high field-emission scanning electron

microscopy (FE-SEM, JSM-6330). The mechanical property (stress versus strain curves) was performed by assembling the rectangular membrane (dimensions: length=40 mm, width=20 mm) with a tensile speed of 2 mm min^{-1} by a texture analyzer (TA-XT. Plus, SMS). The fourier transform infrared (FTIR) spectra was recorded samples using KBr pellets on a PerkinElmer Spectrum GX instrument ($4000\text{-}1000 \text{ cm}^{-1}$). The CPE precursor solution (before polymerization) was dropped on the surface of KBr pellets. The CPE membrane (after polymerization) was finely ground and dispersed into KBr powder-pressed pellets.

The ionic conductivity was acquired by electrochemical impedance spectroscopy (EIS) method with ac amplitude of 5 mV over the frequency range of 100 KHz to 0.1 Hz and a temperature range from $-20 \text{ }^{\circ}\text{C}$ to $80 \text{ }^{\circ}\text{C}$ on a CHI660C Electrochemical Workstation (Shanghai Chenhua). All the electrochemical impedance are tested for three times at each test temperature in order to reduce error ($<3\%$) made by equipment and the average data is calculated and given in curves. The electrochemical stability window was measured by linear sweep voltammetry (LSV) in a three-electrode system, which consisted of a stainless steel blocking electrode as the working electrode and a lithium metal as the reference and the counter electrode ($2.0\text{-}6.0 \text{ V}$, 1 mV s^{-1}). The interfacial stability was determined by symmetrical Li|CPE|Li and Li|CPE|Li cells using EIS measurement ($100 \text{ KHz}\text{-}0.1 \text{ Hz}$, 5 mV), where the CPE and GPE were sandwiched between two lithium electrodes.

Electrochemical experiments were performed by using two-electrode coin cells. High voltage cathode materials $\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ was prepared via the co-precipitation method followed by high-temperature solid-state reaction according to literature [27]. For preparing working electrodes, a mixture of $\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$, carbon black and polyvinylidene fluoride at a

weight ratio of 80:15:5 was dissolved in N-methylpyrrolidinone solution to form slurry. Then, it was spread uniformly on an aluminum foil and dried at 60 °C to remove the solvent. The 2032 cells were assembled by sandwiching the CPE electrolytes, $\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ cathode and a Li metal anode in an argon-filled glove box. For the comparison, the 2032 cells consisting of $\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$, GPE (without Al_2O_3), a Celgard 2400 separator and Li metal were prepared. In the fabrication process, the precursor (the blend of 6 wt% monomer mixtures, 1 wt% initiator and 94 wt% liquid electrolyte) was added into the assembled cells. The assembled cells were settled for 2 h to ensure the precursor solution to be well wetted into the electrodes, and then the cells were heated at 80 °C (30 min) for polymerization [25]. The charge-discharge capacity and cycle ability of the cells assembled with cathode electrode, electrolytes and Li metal anode were estimated at 0.1C (1 C=300 mAh g⁻¹) under a voltage range between 2.0 and 4.8 V by using a CT2001A cell test instrument (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.). The cycle performance of $\text{Li}|\text{CPE}|\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ cells were cycled at a rate of 0.1 C at different cut-off voltages (4.5, 4.6, 4.7 and 4.8 V) and different temperatures (-20, 25 and 50 °C). Three parallel samples were needed in all the experimental testing. Then, the middle one was selected as result. The AC impedance spectra (before and after 100 cycles) of $\text{Li}|\text{GPE}|\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ and $\text{Li}|\text{CPE}|\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ cells were analyzed over the frequency range of 100 KHz-0.1 Hz with ac amplitude of 5 mV.

3. Results and discussion

Fig. 1 The polymerization mechanism of TEGDA and BA (a); The schematic illustration of the flexible CPE (b); The photograph of self-standing CPE membrane (c); FE-SEM images of Al_2O_3 (d) , GPE (e), CPE before charge/discharge (f) and CPE after charge/discharge (g).

Fig. 1a presents the polymerization mechanism of TEGDA and BA. Briefly, the double bonds of the vinyl monomers were opened by decomposition of the initiator to form a monomer radical. Then, the polymer molecular chains gradually increased with the addition of the vinyl monomer chains, and ultimately formed a three-dimensional (3D) polymer backbone [25]. The schematic of the flexible CPE with the addition of Al_2O_3 is provided in Fig. 1b. The Al_2O_3 nanoparticles were incorporated as a functional filler to improve the flexibility of electrolyte membrane. Fig. 1c shows that no rupture was observed when it was twisted around a cylindrical glass rod, indicating that the free-standing electrolyte membrane (thickness: $180 \pm 15 \mu\text{m}$) was highly flexible and bendable. Incorporation of Al_2O_3 nanoparticles could provide mechanical integrity of the gel polymer electrolyte, allowing them to form free-standing membranes even at a low concentration of the copolymer (liquid electrolyte/copolymer=94/6, w/w) compared to that of the polymer used in other research (ETPTA, 15 wt%) [15]. Fig. 1d exhibits the morphology of Al_2O_3 with average particle size of $\sim 20 \text{ nm}$. The polymer matrix as internal scaffolding is well cross-linked to establish 3D framework. Fig. 1e gives the three-dimensional network structure of the GPE, which can be observed at microscopic level. The CPE presents smooth surface and shows that Al_2O_3 has been dispersed in polymer network (Fig. 1f).

Here, the unique morphology of the CPE is expected to play a key role in providing significant improvements in the mechanical bendability and cycle stability under high cut-off voltage. According to the stress-strain curves (Fig. 2), the CPE has shown a maximum stress up to $\sim 1.3 \text{ MPa}$ and, which is much higher than the GPE in previous study ($\sim 0.45 \text{ MPa}$) [25]. Also, the GPE exhibits a tensile elongation of 0.2%, compared to 30% in CPE, indicating much enhanced tensile strength in CPE. The superior mechanical property can be attributed to the Al_2O_3 in the CPE, which

serves as a mechanical buffer to dissipate the stress from stretching strain [24]. Additionally, the well-dispersed inorganic nanoparticles in a polymer matrix could effectively contribute to improving mechanical toughness, owing to the evolution of micro-voids that deconcentrate the external stress [28, 29].

Fig. 2 The stress-strain curves of GPE and CPE.

Fig. 3 FTIR spectra of CPE before and after polymerization.

The copolymerizing reaction of CPE was illustrated by measuring the variation in the FT-IR of the TEGDA-BA monomers before/after polymerization (Fig. 3). After polymerization, the peaks assigned to acrylic -C=C- bonds (1645 cm^{-1}) weakened obviously, indicating that TEGDA-BA was successfully conducted by thermal polymerization. It did not disappear completely owing to presence of partly residual monomers. The peak of the -OH stretching (3645 cm^{-1}) is caused by the absorbing water from the air due to the existence of strong polarity Li ions.

Fig. 4 Temperature-dependent ionic conductivities of CPE (from -20 to 80 °C).

The self-standing CPE membrane with excellent flexibility can be directly assembled into cells without using commercial separators. The ionic conductivities of the GPE and CPE are 1.24×10^{-3} and $3.92 \times 10^{-3}\text{ S cm}^{-1}$ (25 °C), respectively (Fig. 4). The high ionic conductivity is mainly attributed to the ion transfer in the liquid electrolytes, which significantly promotes the lithium ion mobility. Due to the presence of numerous liquid electrolytes, the cross-linked structure provides good mechanical strength and maintains the high conductivity for the CPE. Furthermore, the logarithm

plots of ionic conductivity ($\log \sigma$) exhibit approximately linear relationship with reciprocal temperature (T^{-1}), suggesting that the mechanism of ionic conduction in GPE and CPE follows Arrhenius relationship as below [7]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

where E_a is the activation energy, R the gas constant, T the temperature and σ_0 the pre-exponential factor. According to Eq. (1), the activation energy of the GPE and CPE electrolyte was estimated to be approximately 0.045 and 0.036 eV, respectively. Since E_a is related to the mobility of carriers, lower activation energy would result in faster ionic migration, and thus higher ionic conductivity could be obtained. The enhanced ionic conductivities are associated with the electrolyte uptake due to the enhanced specific surface area from Al_2O_3 nanoparticles, which increases the motivation of lithium ions. The generation of free volume at the surface of the dispersed Al_2O_3 may also contribute to the improved ionic conductivity [15].

Fig. 5a exhibits the AC impedance spectra of GPE and CPE. The interfacial resistance is obtained from a complex plot of the imaginary part of the impedance, Z'' , vs. the real part, Z' (Nyquist plot). The intercept at high frequency on the Z real axis is the bulk electrolyte resistance [7]. The diameter of the semicircle gives the overall interfacial resistance, which takes into account the resistance of charges transfer through a grown solid electrochemical interface (SEI) between lithium metal and solid electrolyte. The interfacial resistance of cell assembled with CPE is considerably lower than that of the cell with GPE, which reveals the benign electrode/electrolyte contact in the interface. The formation processes of SEI in different circumstances have been schematically illustrated (Fig. 5b). The variation of SEI thickness and chemical reactions between SEI components contribute to the instability of interfacial resistance [7]. A poor SEI with high resistance is formed on the

interface between GPE and Li metal, and a larger polarization follows. The variation of interfacial resistance may be attributed to chemical reaction of the components and decomposition of the complicated passivation layer. The decomposition of SEI hinders the intercalation of lithium ions and leads to a large ion concentration polarization. The properties of passivation layer can be affected by combined factors including the chemical structure of polymers, morphology of polymeric networks, surface feature of inorganic fillers and contact between electrodes and the electrolytes. The detailed reactive process and chemical intermediates can be observed and identified by using electron paramagnetic resonance spectroscopy in our future studies. A straight path is provided to facilitate lithium dendrite growth, which increases the risks of internal short-circuit, fire or explosion. A satisfactory SEI with lower resistance generates when CPE is used, and nearly no decomposition is accumulated inside the electrolytes. The addition of the inorganic fillers provides positive effects on the interface stability, which is mainly related to its highly homogeneous particle distribution in the polymeric matrix, and thus leads to a larger polymer-filler interface [7]. This interface structure can be expected to benefit high electrochemical stability and less polarization. Also, owing to the uniform dispersion of Al_2O_3 nanoparticles, the growth of lithium dendrite is substantially retarded in CPE. Due to their high surface area, the Al_2O_3 nanoparticles can effectively help trap residual trace of impurities, such as water, oxygen and decomposed products in the electrolytes, and inhibit the side reaction between the impurities and lithium metals. As a consequence, the growth rate of the passivation layer could be reduced and the compatibility between CPE and Li metal would be improved. This effect of CPE on the improvement of cell safety is very beneficial, wherein the Al_2O_3 nanoparticles act as protective barriers to retard the growth of lithium dendrite on electrode surface [24].

Fig. 5 The AC impedance spectra of GPE and CPE (a) and the schematic illustration of the growth and formation of SEI in GPE and CPE (b).

Fig. 6 exhibits the electrochemical stabilities of $\text{Li}|\text{GPE}|\text{SS}$ and $\text{Li}|\text{CPE}|\text{SS}$ asymmetric model cells. LiPF_6 can endure the high voltage up to 5.1 V [30, 31]. Both the GPE and CPE present stable electrochemical working window ($>5.0\text{V}$), indicating that it is sufficient for the most common LIB electrodes since there is no pronounced chemical decomposition in this potential region. In addition, owing to the TEGDA-BA/ Al_2O_3 framework, the CPE shows the slight improvement in the anodic

stability compared to the GPE. The improvements can be ascribed to the stability enhancement of the electrolyte components, which are more tightly trapped in the CPE than in the GPE. Owing to the homogeneously dispersed Al_2O_3 nanoparticles of large specific surface area, the stable polymer-inorganic filler interface also contributes to enhance the electrochemical stability [7]. The electrochemical stability depends on reduction and oxidation of all the components, such as polymer matrix, liquid electrolyte and filler. The decomposition of the electrolyte is associated to the anodic onset voltage, which is often complicated. Further analysis of the electrochemical stability of the CPE will be discussed in future studies.

Fig. 6 Electrochemical stability window of Li|GPE|SS and Li|CPE|SS cells.

The charge/discharge profiles of the $\text{Li|GPE|Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ and $\text{Li|CPE|Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ cells at the initial cycle (0.1 C/0.1 C, 2.0-4.8V) are exhibited in Fig. 7a. The curve shows a long plateau above 4.5V, which is considered to be the extraction of lithium coupled with simultaneous release of oxygen from Li_2MnO_3 compound [32]. The CPE has

an initial discharge capacity of $\sim 285.7 \text{ mAh g}^{-1}$ and the coulombic efficiency approaches 91.5%, suggesting more comparable to those of GPE ($\sim 228.4 \text{ mAh g}^{-1}$, 85.9%). The discharge capacities of the cells gradually decreased with the increase of cycling numbers (Fig. 7b). After 100 cycles, the retentions of discharge capacities in the GPE and CPE were found to be 75.9% and 76.4%, respectively. The superior cycling ability of the CPE may be attributed to its high ionic conductivity, which probably mitigates the ohmic polarization during cycling. Fig. 7c presents the discharge capabilities of the cells using CPE and GPE as electrolytes at progressively changed rate from 0.1 C to 2 C. Li|CPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cells show slightly reduced discharge specific capacities of $\sim 280.6, 259.1, 226.2, 200$ and 168.2 mAh g^{-1} . In comparison, the discharge capacities of $\sim 236.8, 226.1, 211.6, 178.2$ and 151.2 mAh g^{-1} are obtained in the Li|GPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cells. It demonstrates a very stable capacity retention at each rate, revealing the reversible reaction of lithium ions. The improved rate capabilities are mainly associated with the combination of the enhanced ionic conductivity, high surface area of the Al₂O₃ nanoparticles, good compatibility between the electrolytes and electrodes, and rapid ionic transport.

Fig. 8 provides the cycle performance at different charge cut-off voltages of 4.5, 4.6, 4.7, 4.8 V, corresponding to discharge capacities of 128.9, 233.4, 262.8, 285.7 mAh g^{-1} , respectively. At low charge cut-off voltage (4.5V), the cell leads to a low capacity because partial active mass was not completely utilized. The capacity dramatically increases as the cut-off voltage is increased to 4.8 V. A fraction of unreacted mass is utilized additionally in the extra 0.3 V margin. Due to the wide stability window of the polymer electrolyte, the charging voltage limit of the cell could be safely extended to 4.8 V, which allows more Li ions to participate in the de/intercalation cycles. The steadily stable interface can also increase the cathode cycling capacity.

Fig. 7 The charge/discharge properties of Li|CPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} and Li|GPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cells: initial charge/discharge curves (0.1 C) (a), cycling performance (0.1 C) (b) and rate capability at different current densities of 0.1 C, 0.2C, 0.5C, 1C and 2C (c).

Fig. 8 Cycling stabilities of Li|CPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cell at a rate of 0.1 C at different cut-off voltages (4.5, 4.6, 4.7 and 4.8 V).

The cells present improved discharge capacities at 50 °C (Fig. 9). It can be attributed to the excellent cycling advantage of the fluorine substituted materials [27] and high Li-ion migration rate at high temperature. The capacity fade may be due to the Mn dissolution from Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} at high voltage, which leads to the structural change from pure spinel to a mixed phase of tetragonal Li₂Mn₂O₄ and rock salt phase Li₂MnO₃[33]. At -20 °C, the relative low discharge capacity and retention of discharge capacity are related to the low ionic conductivity of electrolyte and poor conductivity of the material caused by the polarization. The lower ionic conductivity leads to a higher ohmic polarization so that the voltage margin between the working and cut-off potentials is reduced at the initial time period of galvanostatic discharge [34]. In addition, concentration polarization follows during discharge, showing depletion of Li⁺ in the immediate proximity of the cathode particles [35]. All these factors slow the charge transfer kinetics and degrade electrochemical performance of the cells. To enhance the charge/discharge

characteristics of cells at low temperature, methyl acetate (Ma) [36], methyl butyrate (MB) [37], propionitrile (Pn) or butyronitrile (Bn) [34] can be introduced into organic solvent (including EC, DMC and EMC) as a co-solvent.

Fig. 9 Cycling performance of Li|CPE|Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cell at different temperatures (-20, 25 and 50 °C).

Fig. 10a exhibits that EIS of Li|GPE|Li cell continuously grows with increase of cycling number. The straight lines in the low frequency region correspond to the diffusion of lithium ions in Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{7/4}F_{1/4} cathode [24]. In the contrary, the growth of the cell impedance is strongly suppressed in the Li|CPE|Li (Fig. 10b). Such comparison of the interface resistance indicates that the CPE offers benign interfacial compatibility with electrodes during cycling, probably due to the stable electrochemical window and fast ionic transport. The Al₂O₃ nanoparticles, which have high surface area, can effectively hold the liquid electrolytes by physical and chemical interaction and help to trap residual trace of impurities such as water, oxygen or decomposed products of the electrolytes. In the CPE, therefore, the retarded growth in the cell interface

resistance and its high ionic conductivity is believed to have great advantages in the cycling performance.

Fig. 10 Variation in AC impedance spectra (before charge/discharge and after 100 cycles) of $\text{Li}|\text{GPE}|\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ and $\text{Li}|\text{CPE}|\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ cells.

To further understand the mechanism for the improved cycle ability of the CPE, the surface image of the CPE after 100 cycles was performed in Fig. 1g. It suggests that the morphology of 3D framework has been well retained. Neither breakdown of the framework nor peeling-off of the Al_2O_3 was observed, revealing that the Al_2O_3 nanoparticles are stable in the polymer matrix. Here,

the unique morphology of the CPE is expected to play a key role in providing significant improvements in the mechanical bendability and cycle stability under high cut-off voltage. To confirm formation and decomposition of SEI, the surface morphology of $\text{Li}[\text{Li}_{1/6}\text{Ni}_{1/4}\text{Mn}_{7/12}]\text{O}_{7/4}\text{F}_{1/4}$ electrode will be provided in our future study. EDS detection will be carried out to analyze the deposition of manganese and nickel according to literature [38].

4. Conclusion

In summary, flexible, high-voltage and safe CPE has been fabricated based on TEGDA-BA and incorporated Al_2O_3 nanoparticles. The mechanical flexibility and bendability have been improved due to the uniform dispersion of Al_2O_3 particles in polymer network. The CPE has improved ionic conductivity, excellent electrochemical stability, appropriate tensile strength and outstanding charge/discharge performance even at 4.8 V. The results suggest that the CPE hold promising great potential in high-voltage, reliable and long lasting polymer LIBs.

Acknowledgments

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