

New interpenetrating network type poly(siloxane-g-ethylene oxide) polymer electrolyte for lithium battery

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Abstract

We fabricated an interpenetrating network type solid polymer electrolyte with a promising mono-comb type poly(siloxane-g-ethylene oxide) for lithium rechargeable battery. The ionic conductivity of the network polymer electrolyte was closed to 10^{-4} S/cm at near room temperature. Initial cycling result from $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ /polymer electrolyte/lithium metal cell shows excellent cycling characteristics with no capacity fade in a solid electrolyte system. The new polysiloxane polymer electrolyte could be a promising system for large batteries that necessitate long life and inherent safety such as batteries for electric vehicle applications.

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Keywords: Poly(siloxane-g-ethylene oxide); Interpenetrating network; Solid polymer electrolyte

1. Introduction

Solid polymer electrolytes (SPE) for lithium batteries have been investigated for over three decades. In 1978, Armand et al. [1] proposed the use of lithium salt-doped poly(ethylene oxide) (PEO) as an electrolyte for battery applications. PEO polymers doped with lithium salts have acceptable conductivities at 60–80 °C and above, but crystallinity of the polymer limits their room temperature conductivity from 10^{-6} to 10^{-7} S/cm.

Lots of researches have been devoted to lowering the operating temperature of PEO SPE batteries to the ambient region. One of the approaches to improve the ionic conductivity at ambient temperature was to synthesize a highly branched PEO to decrease the crystallization tendency of the PEO main chain and to increase the chain mobility regarding lithium ion transport. Wang et al. [2] prepared hyper-branched solid PEO polymer electrolyte, but its ionic conductivity is low even at 50 °C. A comb-like solid polymer electrolyte has also gained interest. The comb-like polymer blend with PEO and poly[poly(ethylene glycol)ethyl ether methacrylate-co-methyl methacrylate] by Karekar and co-workers [3], was found to have a low ionic conductivity. Their purpose here was to create an amorphous polymer near ambient temperature.

Fully amorphous polymers, which incorporate ethylene oxide units, have shown more promising than the above blends. Two such polymer families are the polyphosphazenes and polysiloxanes. Since the lithium ion transport properties of a polymer depend on complexation of the Li^+ cations by the polymer, the introduction of ethylene oxide ($-\text{CH}_2\text{CH}_2\text{O}-$) units into the above polymer structures provide lithium ion binding sites. The first report of a polyphosphazene polymer electrolyte was poly[bis(methoxy ethoxy ethoxy)phosphazene] better known as MEEP [4]. MEEP, a comb polymer, incorporates four ethylene oxide units onto the highly flexible phosphazene backbone. Allcock and co-workers [4] learned that MEEP was soluble in water, had a glass transition temperature of -84 °C and had a high degree of flexibility as expected. More importantly, though the ambient temperature conductivity was shown to be on the order of 10^{-5} S/cm, nearly two–three orders of magnitude higher than has been observed for most PEO complexes [5]. These results led to the polyphosphazenes being studied as possible polymer electrolytes and, since then, the polyphosphazenes have been functionalized with longer ethylene oxide chains, branched side chains with ethylene oxide and a wide variety of functional groups including sulfonic acids [6], thioethers, sulfones and sulfoxides [7].

Polysiloxanes, also known as silicones, are also inorganic comb polymers, which can have a wide variety of substituents bound to the silicon in the backbone of the alternating silicon and oxygen atoms. Polysiloxanes are superior to

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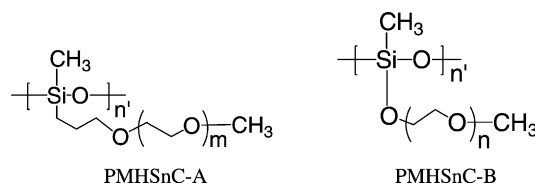
polyphosphazenes with respect to their backbone flexibility, chemical stability, thermal stability, and low toxicity. A variety of organic groups can be bound to the silicon that includes ethylene oxide containing side chains. Although polysiloxanes with oxygen's in the side chains were synthesized as early as 1980, their ionic conductivity was not investigated until 1986 when poly{[methoxy oligo(ethylene)ethoxy]methyl siloxane} was synthesized to study its ionic conductivity [8]. Despite extensive investigations, most techniques used for fabricating solid polymer electrolyte were direct cross-linking between siloxane polymer chains resulting in loss of chain flexibility that is needed for lithium ion transport [9,10]. Recent studies have been focused on the investigation of ionic conductivity according to the number and molecular weight of oligo(ethylene oxide) substituents [11,12].

We have developed comb-like poly(siloxane-*g*-ethylene oxide)s as a base material for an advanced SPE. Although the comb-like polysiloxane showed outstanding ionic conductivity approaching 10^{-3} S/cm at near room temperature, its mechanical strength was not enough for lithium battery application as a separator. In this study, we cross-linked some of poly(siloxane-*g*-ethylene oxide)s through interpenetrating network (IPN) polymerization method to fabricate free standing solid films, and reported their electrochemical data and safety characteristics. The ionic conductivity data of poly(siloxane-*g*-ethylene oxide)s were also presented here.

2. Experimental

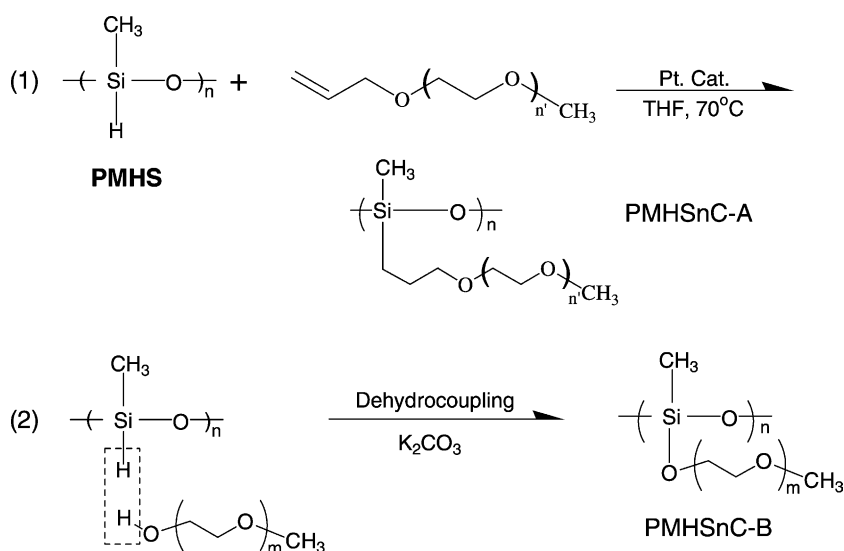
2.1. Synthesis of polysiloxane network SPE

Two mono-comb poly(siloxane-*g*-ethylene oxide), PMHSnC-A and PMHSnC-B (see Scheme 1) were used as a base



Scheme 1. Chemical structures of mono-comb poly(siloxane-*g*-ethylene oxide), where *n* and *m* denote the length of ethylene oxide units.

ionic conducting polymer that is synthesized from commercially available polymethylhydrosiloxane (PMHS). We purchased PMHS from Gelest Inc. The PMHS used is trimethylsiloxy terminated type and has 1400–1800 of molecular weight (M_n). It has 100% MeHSiO according to the data of Gelest Inc. and it is free of –OH group based on IR analysis. The graft reaction of oligo(ethylene oxide) onto Si–H site is described in Scheme 2. Through several stages of solvent washing, mono-comb poly(siloxane-*g*-ethylene oxide)s were prepared. We used interpenetrating network (IPN) polymerization method to prepare solid polymer electrolyte. IPNs are special class of polymer blends in which the polymers exist in networks that are formed when at least one of the polymers is synthesized or cross-linked in the presence of the other. There are two classes of IPNs, one is full IPN and the other is semi-IPN. Full IPN is based on the different polymer systems that are cross-linked to themselves but not to each other. The polymers thus form networks that interpenetrate each other. Semi-IPN is based on combination of cross-linkable and non-reactive linear polymers. The cross-linkable compound forms network and the linear polymer is physically entrapped inside network. Poly(ethylene glycol)dimethacrylate (PEGDMA, Aldrich, $M_n = 550$ g/mol) is used as a cross-linking agent. Lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI) and benzoyl peroxide (Aldrich, radical initiator) were directly dissolved in viscous mono-comb poly(siloxane-*g*-ethylene oxide) and



Scheme 2. Synthesis of mono-comb poly(siloxane-*g*-ethylene oxide).

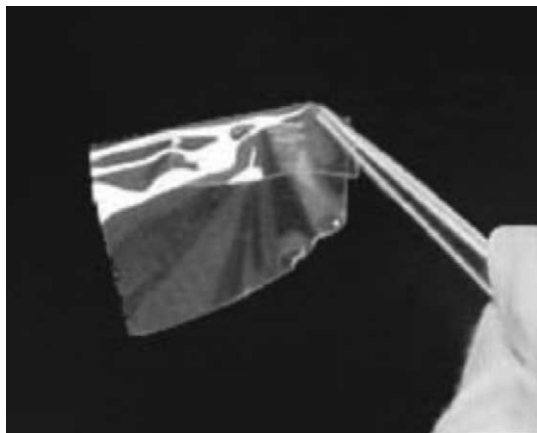


Fig. 1. Photograph of polysiloxane network SPE film.

PEGDMA mixture. The doping ratio, O/Li of siloxane polymer was 32 and that of PEGDMA was 20. The mixture was vacuumed to remove gas pockets and bubbles. The mixture was cast onto a plate and placed in an oven at 70 °C for an hour. The final thickness of the polysiloxane semi-IPN type SPE was controlled <100 μm. The resulting SPE film was transparent and freestanding as shown in Fig. 1.

2.2. Electrochemical and thermal analysis

The ionic conductivities of the poly(siloxane-*g*-ethylene oxide) SPE at temperatures ranging from 25 to 80 °C were obtained from the ac impedance spectra of 2032 button cells. These cells were assembled in a dry room by sandwiching the solid polymer electrolyte between two stainless steel (SS) blocking electrodes. The ac impedance of the cells were measured by using a Schlumberger model 1260 frequency response analyzer connected to Schlumberger model 1286 electrochemical interface and EG&G PAR 273 potentiostat. The 10 mV ac amplitude was applied with a frequency sweep of from 0.1 to 1 MHz. The cells were placed on a heating puck with an upper lid for heat insulation and the cell temperature was controlled within ±0.5 °C by a temperature controller.

The electrochemical stability window of the siloxane SPE was determined using cyclic voltammetry. The cell used for this study was a 2032 button cell assembled by sandwiching the polysiloxane SPE between stainless steel disc used as the working electrode and lithium metal disc used as the counter and reference electrodes.

The thermal stability of the siloxane SPE was investigated using the accelerating rate calorimetry (ARC) system. In this study, a 500 mg of the precursor of the siloxane based polymer electrolyte was placed into a thin-walled stainless steel tube having one end previously sealed by tungsten inert gas (TIG) welding. All ARC samples were prepared in an argon-filled glove box. The ARC sample is next heated to an initial temperature; after a period for system equilibration, the controller next looks for evidence of exothermic reaction. If none is found, the sample is heated to a new temperature and the process is repeated. This heat-wait-

search routine is repeated until exothermic reaction is initiated or until the high temperature limit is reached.

3. Results and discussions

Fig. 2 shows the conductivity data of the base mono-comb poly(siloxane-*g*-ethylene oxide) electrolytes that are mixtures of polysiloxane and lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI). These polymer electrolytes show ionic conductivities above 10⁻⁴ S/cm at room temperature. PMHS3C-B, where the poly(ethylene oxide) is directly attached to the siloxane main chain without a propylene as a spacer between the siloxane and poly(ethylene oxide), shows a ion conductivity ca. 6 × 10⁻⁴ S/cm at room temperature even though its molecular weight is close to 4000 g/mol. B type siloxane structure could increase hydrophilicity and solubility, leading to higher conductivity. These merits come from structural nature and can easily be understood from their chemical bonding structure [13]. It could be found that Si–O bond has more ionic characteristics than Si–C and less rotation barrier; PMHSnC-B structure is more flexible and polar than PMHSnC-A structure.

Semi-IPN method is very useful for fabricating solid polymer electrolyte that can be processed as a film. A cross-linking between poly(siloxane-*g*-ethylene oxide) chains surely reduces whole chain flexibility that is necessary to good conductivity. By using semi-IPN method, PEGDMAs form network to be a film and poly(siloxane-*g*-ethylene oxide)s are entrapped inside the network but still have their flexibility. We did a dissolution test to confirm the solidification with the cross-linked sample in 1 cm³ cube form without lithium salt. The sample was put into hot water for an hour, dried and investigated its weight change, but it was negligible.

Fig. 3 shows the effect of temperature on the ionic conductivity of network type-polysiloxane (NT-PMHS) SPE prepared using PMHS7C-A, where the number of ethylene oxide units is 7.2. NT-PMHS7C-50 and 60 mean that the contents of PMHS7C-A out of NT-PMHS7C SPE

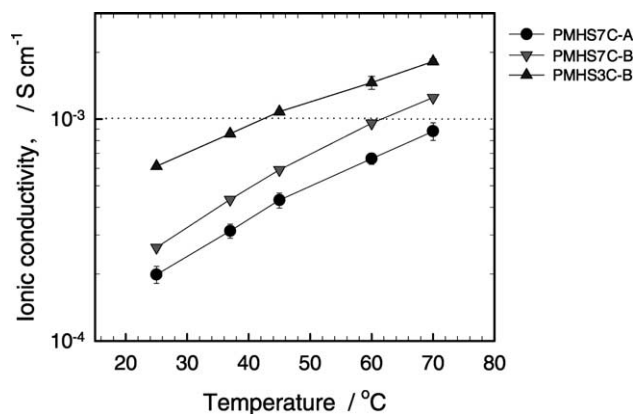


Fig. 2. Ionic conductivity of mono-comb poly(siloxane-*g*-ethylene oxide) polymer electrolytes as a function of temperature.

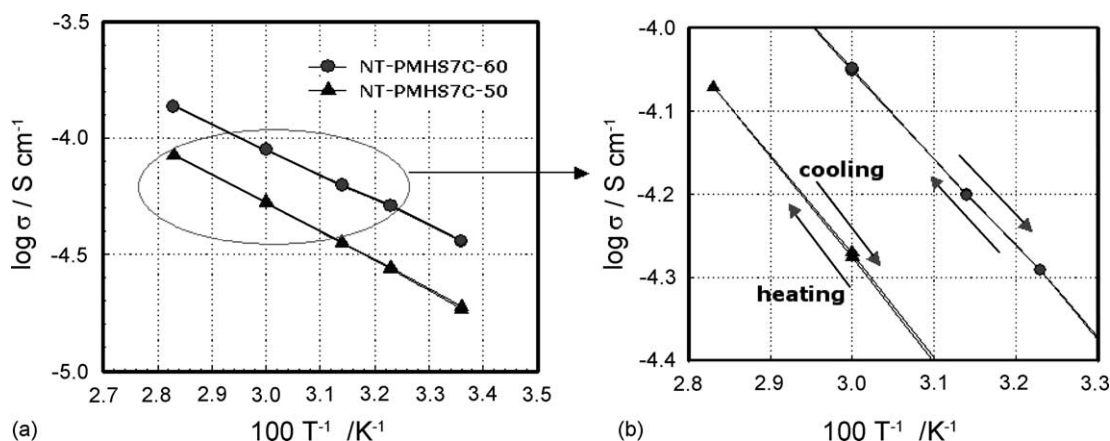


Fig. 3. Ionic conductivity of network type polysiloxane solid polymer electrolytes as a function of temperature: (a) overall ionic conductivity data, and (b) enlarged plot for investigation of thermal hysteresis.

are 50 and 60 wt.%, respectively. The ionic conductivity was measured two times at each temperature point during the heating and cooling to check the thermal hysteresis of the polymer. These polymer electrolytes show ionic conductivities approaching 10^{-4} S/cm at 37°C temperature. This value represents reasonably high ion conductivity at room temperature for a completely solid polymer. The ionic conductivity of the IPN SPE was found to be dependent of the ratio between the mono-comb poly(siloxane-*g*-ethylene oxide) and the cross-linking agents. The IPN SPE with 60% mono-comb poly(siloxane-*g*-ethylene oxide), NT-PMHS7C-60 shows higher ionic conductivity than the one having only 50% mono-comb siloxane. There is also no thermal hysteresis phenomenon in the ionic conductivity during the heating and cooling scan (see Fig. 3b). No thermal hysteresis means the IPN SPE is dimensionally and mechanically stable regardless of operating temperature, here up to 80°C .

The electrochemical stability of the polymer electrolyte is an important factor due to its use with a highly oxidizing (>4 V versus Li/Li^+) positive electrode material in lithium batteries. As PEO has a narrow voltage window, it is generally used in 3 V cell systems, such as lithium–vanadium oxide cathode. NT-PMHS7C-60 SPE shows a stability window of up to 5.1 V versus lithium (see Fig. 4). On anodic sweeps, most PEO electrolytes based on oxyanions show an oxidation peak at $+4.0$ – 4.5 V versus Li^+/Li . It is not clear whether this reflects the oxidation of the anion or electron abstraction from the ether oxygen [14]. Electrochemical stability of PEO is basically dependent upon the sort of lithium salt incorporated. In case of LiTFSI–PEO electrolyte, the window is limited in the cathodic domain by Li^+ reduction and extends in the anodic region up to 4.5 V, enables its use in lithium batteries with a large choice of redox couples as cathode materials [15,16]. The degradation of main chain of polymer is critical in voltage stability. Changing backbone structure of polymer is another way to increase voltage stability. Cross-linking treatment could also enhance the stability. In this study, the major compound,

poly(siloxane-*g*-ethylene oxide)s has siloxane bond as a backbone, LiTFSI–PEO complexation and cross-linked structure enhanced voltage stability synergistically. This result indicates that this SPE polymer can be used in cells that contain high voltage layered lithium nickel or cobalt oxide cathodes combined with graphite anodes rather than vanadium oxide and metallic lithium that is used in PEO polymer systems.

Siloxane main chain of PMHSnC-A and -B polymer is an inorganic material that is thermally very stable and is decomposed by heat with difficulty. Only a few flammable by-products are formed during the thermal decomposition of such polymers because its main chain is a Si–O linkage. The thermal behavior of siloxane based polymer electrolyte was studied using the accelerating rate calorimeter (ARC). The ARC is an adiabatic calorimeter in which heat evolved from the test sample is used to raise the sample temperature and can provide additional information on the energies of activation and other fundamental thermokinetic parameters that are not available using other techniques. We could get an exothermic reaction of a certain chemical system by ARC.

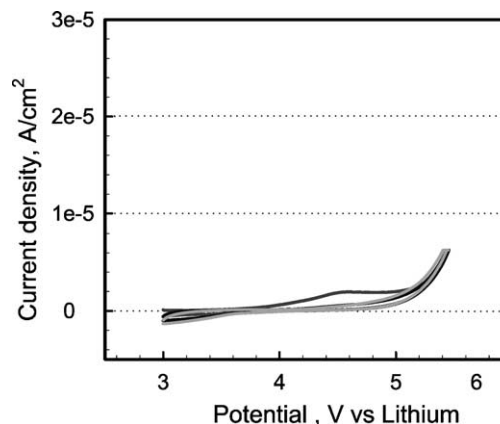


Fig. 4. Cyclic voltammograms for Li metal/NT-PMHS7C-60 SPE/SS cell. Scanning rate was 1 mV/s and the effective surface area of electrodes was ca. 1.6 cm^2 . The thickness of SPE was $85\ \mu\text{m}$.

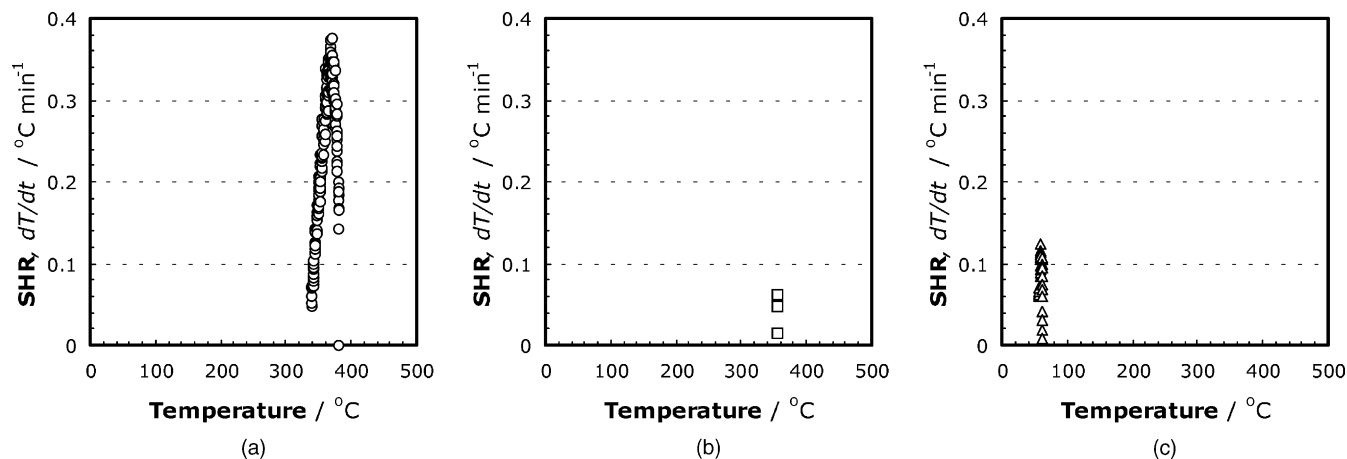


Fig. 5. Measured heat flow from exothermic reaction of test sample, where: (a) PMHS7C-A, (b) PMHS7C-A with LiTFSI, and (c) precursor solution for NT-PMHS7C-60.

In general, the heat generated from thermally unstable materials and exothermic reactions is sufficient to raise its temperature, causing the reaction rate to increase. This in turn may result in an even greater temperature being attained. One of the important data of ARC result is self-heating rate (SHR). ARC detects that SHR at certain temperature until the exothermic reaction is ended. In a battery system, an unexpected temperature increase by the exothermic reaction among components is critical for safety. ARC data is closely related to safety issue of a certain chemical mixture.

Fig. 5 shows the result of self-heating rates of PMHS7C, PMHS7C with LiTFSI and NT-PMHS7C-60 SPE. PMHS7C itself has no major exothermic reaction up to 350 °C (Fig. 5a). The mixture of PMHS7C and LiTFSI shows a very small exothermic peak around 370 °C because of the complexation between PMHS7C and LiTFSI. In the case of precursor solution for polysiloxane network SPE (NT-PMHS7C-60), there is no exothermic peak caused by its thermal degradation, but an exothermic peak owing to the cross-linking reaction and formation of NT-PMHS7C-60 SPE is detected. After the cross-linking reaction, no exothermic reaction of the polysiloxane network SPE (NT-PMHS7C-60) is observed up to 500 °C. Two peaks of Fig. 5(a and b) are shown at similar temperature, but the SHRs are totally different. The reduced exothermic reaction by decomposition and consecutive reactions in Fig. 5(b) was definitely contributed by the complexation or coordination between PMHS7C and LiTFSI. The only difference of composition between Fig. 5(a and b) is LiTFSI. LiTFSI is thermally stable up to 375 °C measured by TGA. At least three ethylene oxides will coordinate with one lithium ion. The coordination could give same effect as that of a partial cross-linking reaction. So, it could reduce the exothermic reaction much at that temperature and that complexation obviously lowered SHR. In the cross-linked system, semi-IPN of Fig. 5(c), poly(siloxane-g-PEO)/LiTFSI (O/Li = 32) is entrapped inside PEO network and that could contribute to

the prevention of rapid decomposition of polymers that generates a heat to increase temperature of sample. In the case of conventional liquid electrolyte, LiPF₆ with carbonate solvents, the exothermic reaction starts below 200 °C. Further studies are under going to investigate the reaction between the current siloxane based network SPE and the charged cathode and anode material to confirm the safety in such cell system.

Fig. 6 shows the specific discharge capacity of the lithium metal/NT-PMHS7C-60 SPE/LiNi_{0.8}Co_{0.2}O₂ cell with the voltage range of 3.0–4.1 V according to the number of cycle. There were no significant side reaction or degradation problems up to 4.1 V for 47 charge–discharge cycles. The specific discharge capacity of the cell is around 130 mAh/g with no capacity fade. Further studies are underway to investigate the cyclic characteristics of this new polymer system with layered lithium nickel oxide cathode and graphite anode.

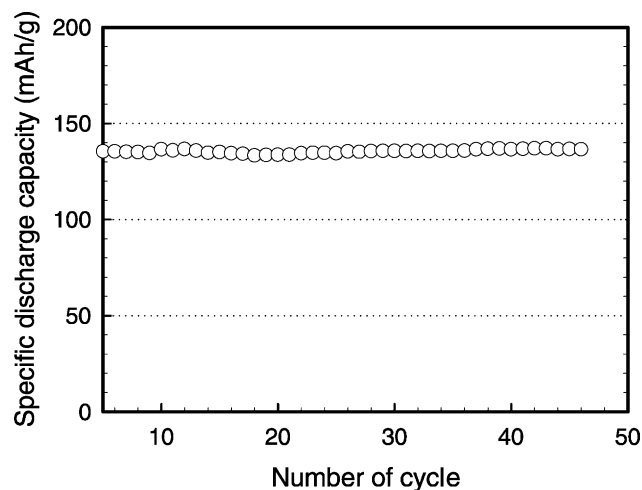


Fig. 6. Specific discharge capacity of the lithium metal/NT-PMHS7C-60 SPE/LiNi_{0.8}Co_{0.2}O₂ cell with the voltage range of 3.0–4.1 V according to cycles.

4. Conclusions

The results of the present study seem to provide some possibility about the use of poly(siloxane-*g*-ethylene oxide) as a base polymer for SPE. Some of the base siloxane polymers show excellent ionic conductivity approaching 10^{-3} S/cm at room temperature. The SPEs based on mono-comb type poly(siloxane-*g*-ethylene oxide)s for lithium battery were successfully fabricated by use of interpenetrating network polymerization method. The poly(siloxane-*g*-ethylene oxide) SPE shows outstanding thermal stability up to 500 °C with an electrochemical stability window of above 4.5 V. The correspondence between the content of poly(siloxane-*g*-ethylene oxide) in the IPN SPE and the ionic conductivity was observed as we expected and it will further be studied in full range of the siloxane content. Initial cycling result from a cell based on the IPN SPE with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and lithium metal shows excellent cycling characteristics with no capacity fade. The new polysiloxane SPE system could be a promising system for large batteries that necessitate long life and inherent safety such as batteries for electric vehicle applications.

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