

Electrochemical properties of all solid Li/Ni₃S₂ cells using polymer electrolyte based on star-shaped siloxane acrylate cross-linker

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All solid Li/Ni₃S₂ cells were assembled with a novel solid polymer electrolyte cured via in-situ chemical cross-linking with siloxane acrylate. Several ether plasticizers with various chain lengths were used to optimize the cycling property of Li/Ni₃S₂ cell. The Li/Ni₃S₂ cell containing the Triethylene glycol dimethyl ether as plasticizer show optimum first charging-discharge and cycling performance, that capacity still maintain 413.32 mAh/g after 20 cycles.

Key words: Ni₃S₂, Solid polymer electrolyte, Electrochemical property.

Introduction

The development of portable electronic devices has created demand on compact lithium batteries, which offer high energy densities [1-3]. Metal sulfides are considered to be potential cathode materials for secondary lithium batteries because of their high theoretical capacity. In particular, nickel sulfides, with the theoretical capacity of 462 mAh/g for Ni₃S₂ and good cycling stability, have drawn attention [4-6]. Moreover, since nickel sulfides exist in nature as minerals as heazewoodite (Ni₃S₂), Ni₃S₂ is abundant and cheap.

Jasinski and Burrows reported that a lithium/nickel sulfides battery showed high coulombic efficiencies (> 50%) in 1M LiClO₄ in propylene carbonate (PC) [7]. In the metal sulfur cell, the metal sulfur undergoes reduction via a series of polysulfides Li₂S_n ($8 \geq n \geq 2$) to ultimately form Li₂S during discharge. As dissolved polysulfides product generates, the physicochemical properties of electrolyte, such as viscosity and conductivity, will change. As a result, among the various candidates for electrolyte, liquid electrolytes with low dielectric constant are widely utilized, dominating high ionic conductivity, low viscosity and good polysulfide solubility. Many researchers focus on ether type electrolyte, such as diethylene glycol dimethyl ether (diglyme) and tetraethylene glycol

dimethyl (tetraglyme) for metal sulfur batteries, which have been found to be an attractive liquid electrolyte for providing high first discharge capacity [8-12]. However, the shortage of liquid electrolyte, such as leakage and crystallization at low temperature, makes it be replaced step by step [13-17].

Traditional gel polymer electrolytes are defined as polymer matrices containing high amount of liquid ionic solvents as plasticizer. Hence, to facilitate the liquid electrolyte filling process, the traditional polymer host has a porous structure by forming temporary physical crosslink, via physical interactions such as crystallites or hydrogen bonds between the chains [18-19]. Compare to the temporary physical cross-linked structure, these chemically cross-linked gel polymer matrices is permanent and remains thermally stable up to the decomposition temperature of the components [19-20]. We employed some linear ether as plasticizers in chemically cross-linked polymer matrices, in order to prepare all solid cells.

In this work, we fabricated all solid Li/Ni₃S₂ cells with the novel solid polymer electrolyte and investigated on the basis of charge and discharge properties. The study will focus on the influences of novel solid polymer electrolytes with different plasticizers on electrochemical property. Some linear ether liquid electrolytes, which had the similar structures except the various chain lengths, were chosen as plasticizers. The cross-linking agent, siloxane acrylate star-shaped prepolymer with oligo (ethylene oxide) acrylate functional group was employed to fabricate polymer matrix.

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Experimental

Preparation of novel gel polymer electrolytes and electrodes

The novel gel polymer electrolyte was prepared as follow:

First, the microporous polypropylene separator (Celgard 2500) was immersed in a homogenous precursor solution consisting of 2,4,6,8-tetramethyl cyclotetrasiloxane (D4A, 30%), different plasticizers (diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether and Polyethylene glycol dimethyl ether, 70%), lithium salts (LiCF₃SO₃), thermal initiator benzoyl peroxide (BPO, weight ratio 2%). The star-shaped siloxane acrylate cross-linking agent (D4A) was synthesized in such process: hydrosilylating poly(ethylene glycol) monoallyl ether with 2,4,6,8-tetramethyl cyclotetrasiloxane and acryloylation, according to previously reported method [21]. The lithium salt concentration theoretically meets the equation $c(\text{EO}) : c(\text{Li}^+) = 10$. Then, after one hour, the microporous polypropylene separator impregnated with solution was sandwiched between glass plate and Al foil and then was cured in convection oven at 90 °C for 30 min. All procedures for preparing the novel gel polymer electrolyte were carried out in a dry-box filled with argon gas.

The Ni₃S₂ electrode was prepared according to the previous method [22]. The cathode film was cut into a disc with 1.0 cm diameter.

Cell assembly

Lithium/Ni₃S₂ polymer cell was assembled by sandwiching the novel gel polymer electrolyte between lithium metal anode and Ni₃S₂ cathode. Whole cell assemblies were operated in a glove box filled with argon gas.

Electrochemical measurements

In order to obtain the interfacial resistances and ionic conductivities, Ac impedance measurements were carried out using IM6 frequency analyzer over the frequency range of 1 mHz - 100 kHz with an amplitude of 10 mV. The charge and discharge cycling tests were conducted at ambient temperature between 0.3 and 3.0 V at a constant current density of 0.1C, using WBCS3000 potentiostat/galvanostat (WonA Tech. Co.).

Results and discussion

Fig. 1 shows photograph of the solid polymer electrolyte with diglyme as plasticizer. Even the novel solid polymer electrolyte encapsulate high amount (70%) of plasticizer, the whole electrolyte was absolutely solid state. The surface of the polymer electrolyte is very smooth, which will improve the interfacial contact between electrode and electrolyte. When the sort of plasticizers varied, the configurations of the novel

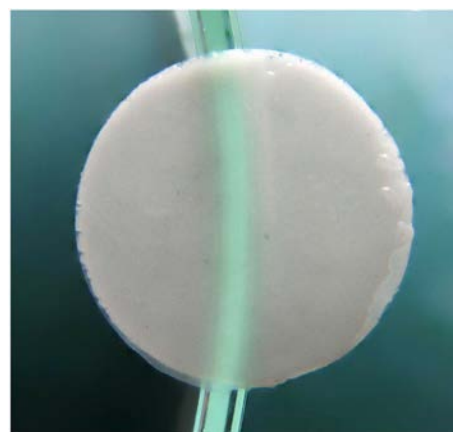


Fig. 1. The photo of polymer electrolyte enhanced by microporous polypropylene membrane.

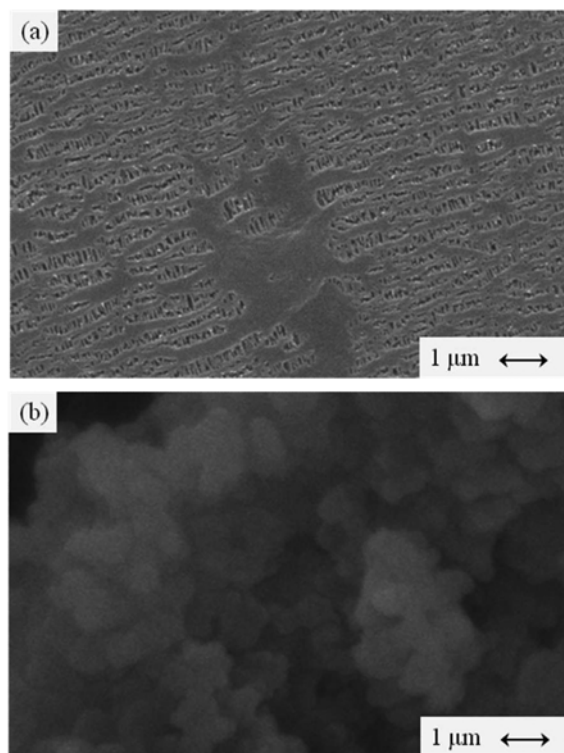


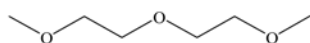
Fig. 2. SEM images of (a) microporous polypropylene membrane and (b) microporous polypropylene membrane filled with gel polymer electrolyte.

polymer electrolytes still remained same. Nevertheless, the mechanical strength of polymer electrolytes increased in direct proportion to the chain lengths of the plasticizers. In the experiment, we observed that the novel solid polymer electrolyte with diglyme is fragile comparing with others.

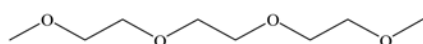
Fig. 2(a) presents the scanning electron micrograph of the pristine microporous polypropylene membrane. The membrane has highly porous structure with nominal thickness of 25 μm and 55% porosity. Fig. 2(b) shows the novel gel polymer electrolyte, all pores of the membrane are filling-up. The particles might be

Table 1. The ionic conductivity of novel gel polymer electrolyte contains varying kinds of plasticizer.

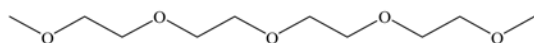
Plasticizer	Ionic conductivity
Diglyme	$1.41 \times 10^{-3} \text{ S cm}^{-1}$
Triglyme	$3.60 \times 10^{-4} \text{ S cm}^{-1}$
Tetraglyme	$5.48 \times 10^{-4} \text{ S cm}^{-1}$
Polyglyme	$6.21 \times 10^{-4} \text{ S cm}^{-1}$



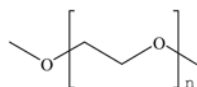
Diethylene glycol dimethyl ether (Diglyme)



Triethylene glycol dimethyl ether (Triglyme)



Tetraethylene glycol dimethyl ether (Tetraglyme)



Polyethylene glycol dimethyl ether (Polyglyme)

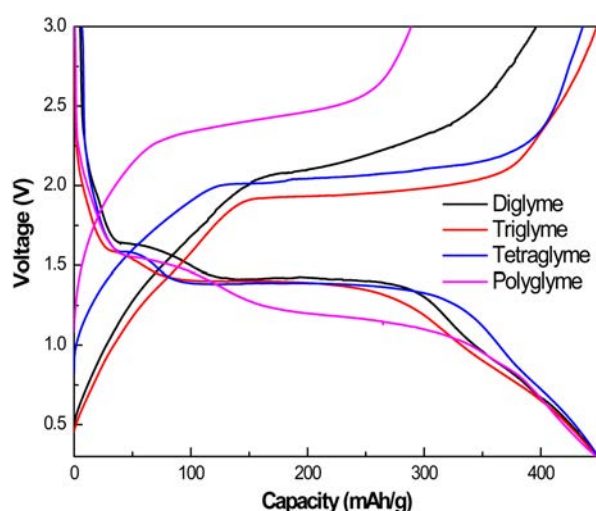
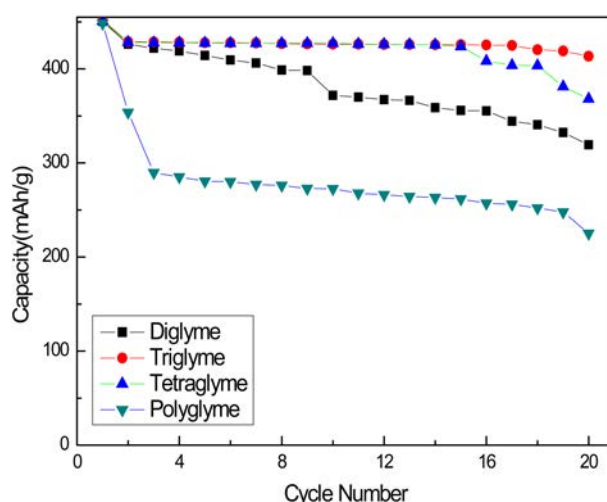
Scheme 1. Chemical structures of linear plasticizers.

the polymer molecule, because the long chain shrunk to form a skein. From the SEM image, the solid polymer electrolyte not only penetrated the pores, but also covered the surface. The thickness of the electrolyte is about 233 μm , which is much larger than polypropylene membrane. The microporous polypropylene membrane has been employed as a dimensional support to enhance the mechanical strength of the novel gel polymer electrolyte.

Table 1 shows the ionic conductivity of SS/SPE/SS cell (SPE: solid polymer electrolyte), which is measured at 25 $^{\circ}\text{C}$. Ionic conductivity was calculated to be S cm^{-1} from the AC impedance result, using the following equation. T_b is the thickness of SPE and A is contact area between electrode and electrolyte. R_b is the bulk resistance of SPE.

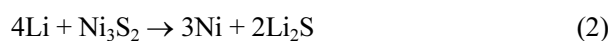
$$\text{Ionic Conductivity} = \frac{T_b(\text{cm})}{R_b(\Omega) \cdot A(\text{cm}^2)} \quad (1)$$

The highest ionic conductivity of the novel gel polymer electrolyte is $1.41 \times 10^{-3} \text{ S cm}^{-1}$, with the diglyme as plasticizer. The ether plasticizer significantly contributes the lithium ions transport in polymer electrolyte, due to the 70% content and vigorous ion conductivity comparing with cross-linked polymer matrix.

**Fig. 3.** First charge-discharge curves at room temperature for Li/ Ni_3S_2 cells with novel gel polymer electrolyte contains varying kinds of plasticizers: (1) diglyme (2) triglyme (3) tetraglyme and (4) polyglyme.**Fig. 4.** Comparison of cycle performance at room temperature for Li/ Ni_3S_2 cells with gel polymer electrolyte contains varying kinds of plasticizer: (1) diglyme (2) triglyme (3) tetraglyme and (4) polyglyme.

The four kinds of plasticizers are structure analogues with different ethylene oxide units, as shown in Scheme 1. The ionic conductivity varies inversely with chain length of the ether plasticizer. The viscosity of plasticizers also increases in direct proportion to the chain lengths, from $0.981 \times 10^{-3} \text{ Pa s}$ to $5.8 \times 10^{-3} \text{ Pa s}$. Therefore, the extent of lithium ions migration, may depend on the viscosity, but dielectric constant (ϵ), which has little influence on.

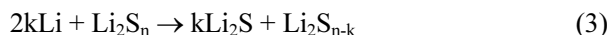
Fig. 3 shows the first charging and discharging curves, with the current density 0.1C. The previous report indicated that the following reactions are possible during the discharge process of Ni_3S_2 . [23]



When the charging-discharging behavior for the cells with novel solid polymer electrolytes is compared, the optimum discharge capacity is 448.6 mAhg⁻¹, in the case of tetraglyme. Moreover, the initial discharge capacities in the case of other plasticizers are similar, which are all closed to the theoretical capacity (450 mAhg⁻¹). The cell based on triglyme shows the highest charge capacity, the diglyme has lower capacity 396.0 mAhg⁻¹, and the polyglyme decreased to only 288.9 mAhg⁻¹. There are two voltage plateaus in the discharge curve, and the main plateau is ca. 1.38 V. On the other hand, there is only one charge voltage plateau. There are high over potential for the cells with triglyme and tetraglyme as plasticizer. Although for diglyme, triglyme and tetraglyme, the numbers of ethylene oxide units diversified slightly, there exists no obvious disparity of property among them. As a result, the first charge curve seemed to be similar, which only depends on the percent of electrode material activation.

Fig. 4 shows the discharge capacities as a function of cycle number in Li/Ni₃S₂ cells with various plasticizers, respectively. After 20 cycles, the cells with triglyme and tetraglyme exhibited the discharge capacities of 413.2 mAhg⁻¹ and 368.0 mAhg⁻¹, respectively. The capacity fade was more obvious for cells with diglyme and polyglyme, actually there is a abrupt slope to 228.13 mAhg⁻¹ in the case of polyglyme at the third discharge.

In Li/ Ni₃S₂ cells, Li₂S_n will form as the cycle carrying on, to cause the viscosity increasing and capacity fading.



The solubility of lithium polysulfide reaction products in the electrolyte has an influence on the electrochemical property of Li/Ni₃S₂ cell, which result in the formation of insoluble, solid reaction products Li₂S₂ and Li₂S depoisting on the cathode film after full discharge.

Due to fixing pasticizers into the network by chemical curing with D4A as a cross-link agent, the novel solid polymer electrolyte serves as a predominant adhesive to electrodes, which lead to excellent capacity rentention. It could be presumed that the electrolyte could still stick very well to the both electrodes, even the cross-linking reaction happened before assmbling the cells. Maintaining good contact between electrodes and this type of solid polymer electrolyte is very important.

In the case of diglyme, the slight decline of the discharge capacity perhaps due to the poor contact. As mentioned before, the polymer with diglyme shows poor mechanical strength. The diglyme molecule may be too small to complex with the branched long chain network, so poor tangle leads to fragility. As a result, the surface of polymer electrolyte perhaps crushed

caused by compression force when assembling a cell.

Whereas, in the case of polyglyme, the cell exhibited worse charge/discharge cycle performance comparing with shorter molecular plasticizers, probably result from descending ionic conductivity and poor flexibility of solid polymer.

Conclusions

In this work, we fabricated Li/Ni₃S₂ cells with novel gel polymer electrolyte, containing 4 kinds of linear plasticizers. The cells using triglyme and tetraglyme have advanced cycle charge-discharge performance at ambient temperature, comparing to diglyme and polyglyme, which capacities fade during cycle process. The ether plasticizers, which had similar structure but different chain length, are promising additives to enhance the chemical property at ambient temperature for Li/Ni₃S₂ batteries.

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