



A solid polymer electrolyte based on star-like hyperbranched β -cyclodextrin for all-solid-state sodium batteries

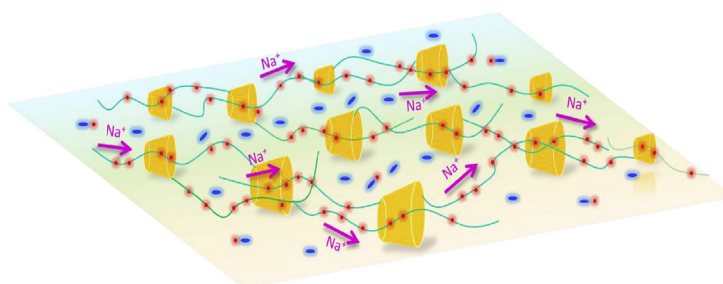
Suli Chen, Fan Feng, Yimei Yin, Haiying Che, Xiao-Zhen Liao*, Zi-Feng Ma**

Shanghai Electrochemical Energy Devices Research Center, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

HIGHLIGHTS

- A novel star-like hyperbranched β -CD is designed as the solid polymer electrolyte.
- H- β -CD maintains considerable mechanical properties at even elevated temperature.
- H- β -CD shows an excellent ionic conductivity of $1.3 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C .
- H- β -CD has good electrochemical compatibility with Na metal electrode.
- Na/NaFM cell using H- β -CD exhibits superior reversibility and cycling stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Solid polymer electrolyte
Hyperbranched β -cyclodextrin
Sodium batteries
 $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$
All-solid-state battery

ABSTRACT

A star-like hyperbranched β -cyclodextrin is designed and synthesized for the solid polymer electrolyte of all-solid-state sodium batteries by grafting β -cyclodextrin with multiple oligo(methyl methacrylate)-*block*-oligo(ethylene glycol) methyl ether methacrylate short chains. Complexing this star-like hyperbranched β -cyclodextrin with sodium trifluoromethanesulfonate salt leads to a self-standing, transparent, and flexible solid polymer electrolyte film. It is found that this solid polymer electrolyte exhibits superior thermal stability, excellent mechanical properties at the even elevated temperature and good interfacial stability against Na metal electrode. Especially, ascribing to the unique three-dimensional structure of the star-like hyperbranched β -cyclodextrin, a solid polymer electrolyte formed with the optimized star-like hyperbranched β -cyclodextrin containing 69.3 wt. % oligo(ethylene glycol) methyl ether methacrylate shows an ionic conductivity of $1.3 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C and a wide electrochemical window of 5.2 V vs. Na^+/Na , which are superior to those of the previously reported solid polymer electrolytes. The all-solid-state Na/Na $\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell shows high first discharge capacity (102.4 mAh g^{-1} at 0.1C), good reversibility and excellent cycling performance (with 87.8% capacity retention after 80 cycles at 0.1C) at 60°C . All the results indicate that the star-like hyperbranched β -cyclodextrin is a promising polymer for the solid polymer electrolyte of all-solid-state sodium batteries.

1. Introduction

Rechargeable sodium ion batteries (SIBs) have attracted

considerable attention, especially in the large scale energy storage applications, because of high abundance of sodium element in the earth's crust, and their moderately high voltage and cost efficiency compared

* Corresponding author.

** Corresponding author.

E-mail addresses: liaoxx@sjtu.edu.cn (X.-Z. Liao), zfma@sjtu.edu.cn (Z.-F. Ma).

with the lithium ion batteries [1–4]. The electrolyte plays a critical role in the batteries by transporting the ions accompanied with the electrode reactions [5]. The liquid electrolytes normally suffer from some problems such as narrow electrochemical window and flammability. These drawbacks not only limit application of the SIBs, but also restrict the energy density of the SIBs and the use of high voltage cathode materials such as $\text{Na}_2\text{CoPO}_4\text{F}$ and $\text{Na}_2\text{Fe}(\text{SO}_4)_3$ [6,7]. Moreover, the liquid electrolytes are poorly compatible with conventional cathode and anode materials in the chemical stability [8,9]. In contrast, solid electrolytes well meet the safety requirement, and may allow the use of metallic Na anode and high-voltage cathode materials to achieve high energy density and long cycle life because of their favorable mechanical property in resisting the penetration of sodium dendrites and the volume change of electrodes during the charge/discharge process [10,11].

The solid state electrolytes are classified to two categories of solid polymer electrolytes (SPEs) and inorganic solid electrolytes. In many aspects, the SPEs are advantageous over the inorganic solid electrolytes, including the flexibility of dimensional shape to enable effective contact with the electrodes, the simplicity of film-making process, and the mechanical strength to resist sodium dendrite penetration and the volume change of electrodes [12–16]. In the present, most of studies on the SPEs for SIB applications are focused on poly (ethylene oxide) (PEO), poly acrylonitrile, and polyvinyl alcohol [17–21]. These polymers generally gave low ionic conductivity ($< 10^{-6} \text{ S cm}^{-1}$ at room temperature), which cannot satisfy the requirement for practical applications. Main reasons for low conductivity are the high glass transition temperature and high crystallinity of these polymers. It is known that in the SPEs, the ions are conducted through the movement of polymeric segments, which occurs mainly in the amorphous regions [12,22]. Therefore, several efforts have been taken to reduce the crystallinity of polymers, for example, adding inorganic particles or liquid plasticizers into the polymer matrix, copolymerizing with other monomers, and blending with other polymers. Although the above approaches made improvement in some extent, the ionic conductivity was still not high sufficient to meet the practical applications [23–26]. Alternately, using a branch-structured or a star-like polymer has been reported to be an effective way for improving high ionic conductivity of the SPEs because such polymers are intrinsically amorphous, which favors the movement of polymeric segments and consequently enhances the ionic conductivity [27–29].

Star-like hyperbranched polymers feature many short oligomeric chains radiating from the center core and amorphous phase structure, which are proven to favor the ionic conduction in the solid polymer electrolyte (SPE) matrix [30–32]. Furthermore, mechanical and electrochemical properties of the SPEs can be improved by modifying the chemistry and/or the length of the side oligomeric chains. Of particular interest, β -cyclodextrin (β -CD) is a natural macrocyclic compound consisting of seven glucose units that are head-to-end linked into a ring through the oxygen atoms at the 1- and 4-positions. The β -CD has a specific steric structure of truncated conical shape with an inner cavity, and each molecule contains 21 substitutable hydroxyl groups. These features provide plenty of opportunity to design star-like polymers [33–35]. Moreover, the rigid β -CD inner cavity structure provides additional free-volume for the movement of polymeric segments, which further increases ionic conductivity while retaining mechanical strength.

With the above knowledge in mind, in this work we designed and synthesized a star-like hyperbranched polymer by grafting β -CD with multiple oligo(methyl methacrylate)-*block*-oligo(ethylene glycol) methyl ether methacrylate (PMMA-*b*-PPEGMA) short chains via the atom transfer radical polymerization (ATRP). The procedures of synthesizing star-like hyperbranched β -cyclodextrin (H- β -CD) consisted of three steps: (1) functionalizing β -CD to give a bromoisobutryl-terminated cyclodextrin (21Br-CD) initiator, (2) grafting the first PMMA block to form CD-(PMMA)₂₁ intermediate, and (3) linking the second PPEGMA block to the end of CD-(PMMA)₂₁ segment, as shown in Scheme 1.

Complexing H- β -CD with NaSO_3CF_3 in tetrahydrofuran (THF) solvent gave a clear SPE solution, which was subsequently casted onto a polytetrafluoroethylene plate to form a free-standing, transparent, and flexible SPE film. The H- β -CD based SPE was studied in terms of the thermal stability, mechanical properties, ionic conductivity, electrochemical window and interfacial stability, and finally the all-solid-state Na/NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cell was assembled by using a SPE film as the separator and evaluated in terms of the rate capacity and cycling stability.

2. Experimental section

2.1. Materials

β -Cyclodextrin (β -CD, 97%), 2-Bromoisobutryl bromide (BIBB, 98%), poly (ethylene glycol) methyl ether methacrylate (PEGMA, Mn = 500), copper(I) bromide (CuBr, 98%), N,N,N',N'',N''-penta-methyldiethylenetriamine (PMDETA, 99%) and anhydrous 1-methyl-2-pyrrolidinone (NMP, 99.5%) were purchased from Sigma-Aldrich and used as received unless otherwise noted. β -CD was recrystallized with water three times and dried under vacuum at 100 °C prior to use. Copper (I) bromide was purified by washing with acetic acid and methanol three times, and dried in vacuum. Methyl methacrylate (MMA, 99%), polyethylene oxide (PEO, Mw = 10⁶), succinonitrile (SN), and sodium trifluoromethanesulfonate (NaTf, 98%) were obtained from Aladdin Chemical Reagent Co., Ltd, Shanghai, China. MMA was passed through a column of activated basic alumina to remove inhibitors before using. PEO was dried overnight at 60 °C under vacuum prior to use. NaTf was dried at 120 °C under vacuum for 24 h before using. Anisole (Sinopharm, 98%) was distilled over CaH₂ under reduced pressure prior to use. Tetrahydrofuran (THF, Sinopharm, 99%) was refluxed over sodium wire and distilled from diphenylmethanone solution. All other reagents were analytical grade and provided by the Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of 21Br-CD

21Br-CD core was synthesized according to previously published literature with little modification [36]. Typically, β -CD (1.14 g) was dissolved in 10 mL of anhydrous NMP in a schlenk flask under N₂ protection and cooled to 0 °C. 5.8 mL of BIBB was then slowly added to the β -CD solution under magnetic stirring. The reaction temperature was naturally increased to room temperature after stirring for 30 min at 0 °C, and the solution was reacted at ambient temperature for 24 h. Subsequently, the flask was placed in vacuum oven overnight to concentrate the solution. The obtained product was diluted with 10 mL of CH₂Cl₂ and then washed with saturated sodium bicarbonate solution and distilled water. The obtained organic layer was dried with anhydrous sodium sulfate (Na₂SO₄) and concentrated by rotary evaporator, and then the syrup-like product was precipitated into cold n-hexane to obtain the resulting white precipitate, dried under vacuum at room temperature. ¹H NMR [400 MHz, CDCl₃, δ (ppm), TMS ref.]: 1.9 (126H, CH₃), 3.5–5.4 (49H, sugar protons).

2.3. Synthesis of CD-(PMMA)₂₁

CD-(PMMA)₂₁ with 21 arms was synthesized by ATRP method using above 21Br-CD as a macro-initiator and CuBr/PMDETA as a co-catalyst. Typically, 21Br-CD (0.2 g, 1 mmol initiating sites), PMDETA (0.208 g, 1 mmol), CuBr (0.142 g, 1 mmol), and MMA (5.31 mL, 59.3 mmol) were dissolved in 41 mL of anisole in a schlenk flask, and then the flask was degassed by three freeze-pump-thaw cycles. The reaction system was sealed and reacted at 80 °C under magnetic stirring. After 2 h, the reaction was stopped by exposing the catalyst to air and cooling the system in liquid nitrogen. Subsequently, the obtained solution was diluted with 20 mL of THF and passed through a neutral

Download English Version:

<https://daneshyari.com/en/article/7724654>

Download Persian Version:

<https://daneshyari.com/article/7724654>

[Daneshyari.com](https://daneshyari.com)