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An All-solid-state and All-organic Sodium-ion Battery based on Redox-active Polymers and Plastic Crystal Electrolyte

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ABSTRACT

A solid state Na^+ electrolyte is developed by dissolving Na^+ salts into the organic crystal succinonitrile, which exhibits a high ionic conductivity of $\sim 10^{-3}$ S cm^{-1} at room temperature and a wide electrochemical window of >3 V. Based on this solid-state electrolyte, an all-organic Na–ion battery is constructed by use of poly(aniline/o-nitroaniline) (P(AN-NA)) cathode and poly(anthraquinonyl sulfide) (PAQS) anode. This solid-state battery works well with an open circuit voltage of 2.4 V and can be cycled at considerable high rate of > 800 mA g^{-1}, showing a competitive performance to the organic solvent Na-ion batteries.

1. Introduction

Rapid development of renewable electricity such as solar arrays and wind farms requires safe, affordable and effective electric energy storage (EES) systems that can integrate these intermittent energy sources into the current electric grid. Many types of rechargeable batteries from conventional lead-acid and nickel-cadmium batteries to advanced Li-ion batteries have been tried for grid-scale EES application, but all of them suffer either from cost and resource restrictions or from environmental constraints. [1,2] Na ion batteries appear to be a very attractive alternative to the current batteries for EES application because of their low cost, material abundance and environmental benignity. Despite a number of Na-ion batteries have been recently developed to demonstrate acceptable electrochemical capacity and cyclability, they are mostly based on transition-metal compounds and liquid electrolytes. [3,4] If Na-ion batteries could be built in all-solid-state at room temperature, it would greatly increase their safety and reliability for EES applications.

The critical challenge for realizing all-solid-state Na-ion batteries is to have a solid electrolyte with sufficient Na^+ ion conductivity and low interfacial resistance at ambient temperature. Though many types of solid electrolyte Na^+ conductors such as NASICON-type glass ceramics [5–8] and sulphide-based electrolytes [9] have been developed, these electrolytes can only work at high temperature but fail to conduct Na^+ ions at room temperature. Thus, the development of highly conductive, electrochemically stable and solid-state Na^+-conductors still remains a challenge.

Plastic crystal electrolytes (PCEs) are a new type of fast ion conducting solids, which are usually formed by dissolving ionic salts into a polar organic molecular solid. In past decade, various plastic crystal electrolytes have been developed for rechargeable Li batteries, [10–12] fuel cells [5–7,13] and dye-sensitized solar cells; [14] however, plastic crystal Na^+-ion conductors have not been reported for Na battery application. If a fast Na^+ conducting PCE could be developed, it would be greatly favorable for realizing room temperature all-solid-state Na-ion batteries.

To construct a Na^+ conducting PCE, we selected succinonitrile ($N{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}C{\equiv}N$, SCN) as a solid solvent and doped Na^+ salts into the organic solid matrix. The thus-prepared Na^+-PCEs exhibited an ambient-temperature, solid-state conductivities as high as 10^{-3} S cm^{-1}, reaching the values of organic liquid electrolytes in Na-ion batteries. Moreover, these fast Na^+ conductors also display a plastic phase in a quite wide temperature range from −35 °C to 62 °C, a wide electrochemical window from 1.3 V to +4.9 V (vs. Na/Na^+), and a good mechanical flexibility, thus enabling their use for Na-ion batteries.

Based on this new solid electrolyte, we constructed an all-solid-state and all-organic Na ion battery using redox-active polymeric

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cathodes and anodes. Herein, we report the fabrication and conductivity behavior of the Na^+ conducting PCEs and describe the electrochemical performances of the all-solid-state Na-ion battery assembled with aniline-nitroaniline copolymer as cathode and poly (anthraquinonyl sulphide) as anode. Such a Na-ion battery can work well an average voltage of 1.6 V and deliver a high reversible capacity of 196 mAh g^{-1} (in terms of anodic mass) at a current density of 50 mA g^{-1} with a 82% capacity retention after 50 cycles. Surprisingly, this solid-state battery can also have a strong rate capability at high rates of >800 mA g^{-1} at room temperature, similarly as organic solvent Na-ion batteries.

2. Experimental

The Na^+-PCEs were prepared by dissolving sodium salts into a melt of SCN at 65 °C under argon atmosphere for 1day and then casting the melt into transparent film at slow cooling. The P(AN-NA) and PAQS used in this paper were prepared in the same ways as described in our previous works,[15,16] respectively. P(AN-NA) was synthesized via chemical oxidative polymerization.[15] A typical experimental procedure was to add dropwise ammonium persulfate (10 mmol in 0.4 M H_2SO_4 10 mL) into a mixed solution of 40 mL 0.4 M H_2SO_4 and 30 mL ethanol containing aniline (5mmol) and o-nitroaniline (5mmol) at vigorous stirring in ice-bath for 2 hours. Once the polymerization took place with the appearance of a dark green suspension, the suspension was then stirred at room temperature for 2 days. The copolymer was obtained by filtering and rinsing the solid product several times with distilled water and ethanol, and then immersing in hydrazine for 24 h, thus giving a leucoemeraldine base form of P(AN-NA). PAQS was synthesized by a polycondensation reaction of Na_2S and1,5-Dichloroanthraquinone.[16] Anhydrous Na_2S was obtained by removing the hydrated water from $Na_2S·9H_2O$ (Lingfeng Chemical reagent co., Ltd, Shanghai, China) through azeotropic dehydration in benzene at 135 °C. After evaporation of benzene, a stoichiometric quantity of 1,5-Dichloroanthraquinone (Alfa Asser) and N-methyl-2-pyrrolidone (NMP) was added into the mixture and then refluxed at 150 °C for 10 h under magnetic stirring. After the reaction was completed, the solid was filtered, then washed alternately with de-ionized water and acetone, and finally dried in vacuum oven over night at 60 °C.

Differential Scanning Calorimetry (DSC) was conducted on a NETZSCH DSC 200 PC differential thermal analyzer (Germany) in N_2 at a scan rate of 10 °C min^{-1} from −20 to 80 °C. Conductivity was tested with a DDS-307 conductivity meter (Lei-ci, Shanghai).

The electrochemical measurement of P(AN-NA) and PAQS materials were separately examined by use of three-electrode cells with Ag/AgCl as a reference electrode. The P(AN-NA) cathode was prepared by rolling a mixture of 70 wt% active material, 20 wt% ketjen black carbon and 10 wt% polytetrafluoroethylene into a thin film. The PAQS anode was consisted of 40 wt% active material, 50 wt% ketjen black carbon and10 wt% binder. The mass loading of the active material for the cathode and anode films was ~4 mg cm^{-2}. The electrolyte was 5 mol% $NaClO_4$ in SCN and a microporous separator (Celgard 2400) infiltrated by the Na+-PCEs is used to avoid short circuit under the pressure. All the cells were assembled in a glove box with water/oxygen content lower than 1 ppm and tested at room temperature. The galvanostatic charge/discharge tests were performed on a LAND cycler (Wuhan Kingnuo Electronic Co., China). Cyclic voltammetric measurements were carried out at a scanning rate of 0.5 mV s^{-1} using a CHI600c electrochemical workstation (ChenHua Instruments Co., China). Electrochemical impedance spectra (EIS) of the charged full cell were recorded by the Impedance Measuring Unit (IM 6e, Zahner) with oscillation amplitude of 5 mV at the frequency range from 100 m Hz to 100 k Hz.

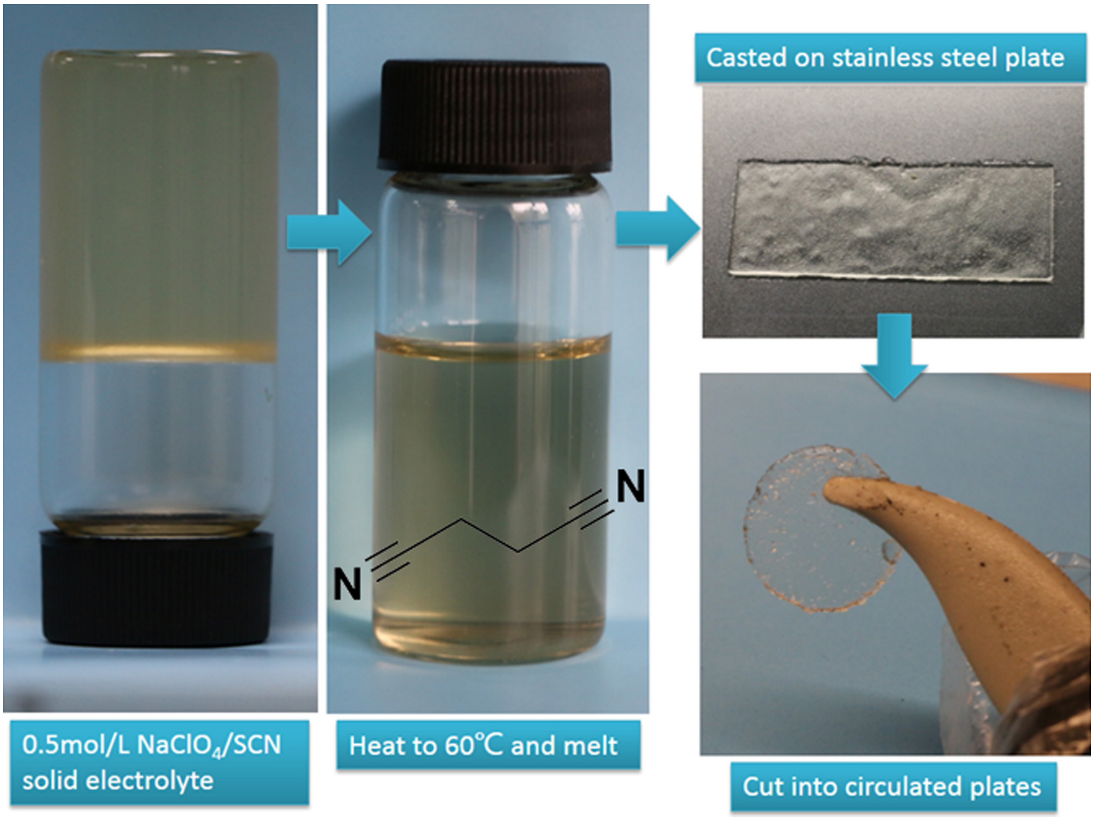

Fig. 1. Preparation process of the Na-SCN PCEs.