

The short-term cycling properties of Na/PVdF/S battery at ambient temperature

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Abstract The Na/PVdF/S cells were composed of solid sodium, sulfur, and polyvinylidene fluoride–hexafluoropropene (PVdF) gel polymer electrolyte. The PVdF polymer electrolyte was prepared from tetraglyme plasticizer and NaCF_3SO_3 salt, and its electrochemical properties were studied using CV and impedance analysis. The interfacial resistance between sodium and polymer electrolyte increase with storage time, which might be associated with passivation layer. Solid-state sodium/sulfur cell using a PVdF gel polymer electrolyte has been tested. The Na/PVdF/S cell with 0.288 mA cm^{-2} shows a high discharge capacity of 392 mAh g^{-1} and 36 mAh g^{-1} after 20 cycles. The cycle performance of Na/GPE/S cell operating at 25°C is worse than Na/S cell at a high temperature.

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Introduction

A lot of researches of sodium/sulfur battery have been performed for the last several decades because it had high theoretical energy density (760 W h/kg) and low material cost [1]. The sodium/sulfur battery could be applied for the electric storage system, electric vehicles, and so on [2]. One of the severe problems of the sodium/sulfur battery was high operating temperature above 250°C , which could induce explosion and corrosion because of molten sodium, sulfur, and polysulfides. In order to decrease the operating temperature, sodium ion type batteries have been studied [3]. However, the energy densities of the sodium ion batteries were much lower than high-temperature sodium/sulfur cell. Recently, lithium/sulfur battery has been studied extensively because of high energy density [4]. However, there were only a few studies on the sodium/sulfur battery operated at room temperature [5–7].

Wang et al. [8] reported Na/S batteries using composite sulfur (CS) cathode with sulfur embedded in a polymer matrix at room temperature. The Na/CS battery could be discharged at high utilization in NaClO_4 with ethylene carbonate (EC) and dimethyl carbonate (DMC) at a weight ratio of 2:1. The first discharge capacity of Na/CS battery showed a 655-mAh g^{-1} capacity in a current density of 0.1 mA cm^{-2} and capacity of 500 mAh g^{-1} was maintained after the 18th cycle, which showed almost 100% coulombic efficiency. Polymer electrolytes are attractive because of the flexibility, safety, and compaction [9]. There were some investigations of polymer electrolytes with sodium ion such as PEO with sodium trifluoromethane sulfonate

(NaCF_3SO_3), sodium (bis)trifluoromethane sulfonate imide ($\text{Na}(\text{CFSO}_2)_2\text{N}$), sodium trifluoroacetate (NaCF_3COO), sodium nitrate (NaNO_3), and so on [5–7, 10, 11]. Park et al. [12] reported an all-solid state Na/S battery using poly ethylene oxide (PEO) polymer electrolyte operated at 90 °C. PEO polymer electrolyte was prepared by dissolving salts of PEO and NaCF_3SO_3 in acetonitrile at a weight ratio of 9:1. The all-solid state Na/PEO electrolyte/S battery showed the first discharge capacity of 505 mAh g^{-1} in a current density of 0.144 mA cm^{-2} and a 10th discharge capacity of 166 mAh g^{-1} at 90 °C. Tian et al. [13] reported that polyvinylidene fluoride–hexafluoropropene (PVdF) gel electrolyte had a high Na^+ conductivity of 10^{-4} S cm^{-1} at ambient temperature. Ryu et al. [14] reported electrochemical properties of the Li/PVdF/S cell using PVdF gel polymer electrolyte. The PVdF gel polymer electrolyte was prepared using 0.5 M LiCF_3SO_3 , tetraglyme as plasticizer, 5.5% Kynar 2801, and PVdF powders in THF solvent in an argon-filled glove box. The Li/PVdF/S cell showed the first discharge capacity of 1268 mAh g^{-1} corresponding to 78% utilization of theoretical value. Park et al. [15] reported a Na/S battery using a PVdF polymer electrolyte operated in low current density at room temperature. The PVdF gel polymer electrolyte was prepared from PVdF powers, tetraglyme, and NaCF_3SO_3 in acetone. The Na/PVdF/S cell had the first discharge capacity of 489 mAh g^{-1} . The discharge capacity decreased severely during cycling. Most of the studies for Na/S battery at ambient temperature have been tested in low current density for electrochemical properties.

In this study, the PVdF gel polymer electrolyte with tetraglyme plasticizer and NaCF_3SO_3 is prepared. Suitability of PVdF polymer electrolyte for Na/S batteries is evaluated. The electrochemical properties of Na/PVdF polymer electrolyte/S battery is tested in a high current density of 0.288 mA cm^{-2} .

Experimental

Preparation of electrodes

Elemental sulfur powder (–200 mesh, Aldrich Co.) and poly ethylene oxide (PEO, M_w 4×10^6 , Aldrich Co.) were dried under vacuum at 60 °C for 24 h and acetylene black (99.9%, Alfa Co.) was dried under vacuum at 90 °C for 24 h. Sulfur electrode was prepared from 70 wt.% elemental sulfur powder, 20 wt.% acetylene black and 10 wt.% PEO in acetonitrile (99.5%, Junsei Chemical Co.) solution and then it was mixed for 2 h by attritor ball-milling. Mixed slurry was spread uniformly onto a glass dish and dried in air to evaporate the solvent. Films were then placed in a vacuum oven (5×10^{-4} Torr) and heated at

60 °C for 24 h. Sodium electrode was prepared by cutting from a sodium ingot (99.95%, Aldrich Co.) in an argon gas atmosphere.

Preparation of polymer electrolyte

Polyvinylidene fluoride–hexafluoropropene (PVdF–HFP, M_w 1.54×10^5 , Kynar2801, Elf Atochem Co.) and sodium trifluoromethane sulfonate (NaCF_3SO_3 , Aldrich Co.) were dried under vacuum at 90 °C for 24 h. Tetra ethyleneglycol dimethyl ether (Tetraglyme, Aldrich Co.) and acetone (99.9%, Aldrich Co.) were directly used without a special pretreatment. PVdF–HFP–Tetraglyme– NaCF_3SO_3 gel polymer electrolyte was prepared by dissolving PVdF–HFP, Tetraglyme and NaCF_3SO_3 in acetone at a weight ratio of 3:6:1 [8]. The solution was stirred for 24 h and then cast onto a glass dish and dried to evaporate the solvent. All preparation, casting, and evaporation of the gel polymer electrolyte were carried out in a glove box under argon atmosphere.

Electrochemical evaluation

The cells were assembled under an argon atmosphere and the operating temperature of the cell was room temperature (25 °C). The stainless steel (SS) blocking cell was assembled by sandwiching the PVdF gel polymer electrolyte between two sodium electrodes. The ac impedance measurements are measured by CMS100 electrochemical measurement system (Gamry Instruments Inc.) and analyses of Nyquist plots were conducted using CMS300 electrochemical spectroscopy software. The data were collected over a frequency range from 10 mHz to 100 kHz. Na/PVdF/S and SS/PVdF/SS cells were subjected to cyclic voltammetry (CV) measurements (WBCS3000, WonA Tech. Co) with a constant sweep rate of 0.1 mV s^{-1} in a voltage range from –2.5 V to 2.5 V. The cell was charged and discharged at room temperature (25 °C) in the constant current densities of 0.288 mA cm^{-2} .

Results and discussion

Electrochemical properties of PVdF polymer electrolyte

The cyclic voltammogram (CV) suggests the existence of electrochemical equilibrium between the sodium metal and the Na^+ ions in polymer electrolyte. The electrochemical reversibility of the Na/Na^+ couple is important as an essential requirement for a possible application in a solid-state sodium battery using the polymer electrolyte. Fig. 1 shows the cyclic voltammograms of the symmetrical cells such as SS/PVdF/SS and Na/PVdF/Na with a scan rate of

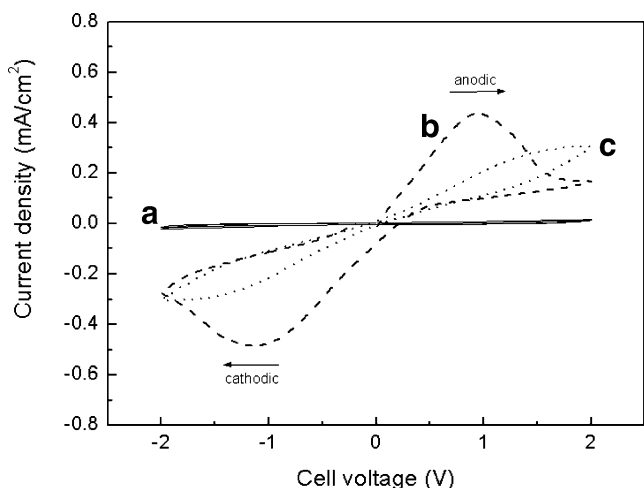


Fig. 1 Cyclic voltammogram curves at 25 °C under a scan rate of 10 mV s⁻¹: (a) 1st cycle of SS/PVdF/SS, (b) 1st cycle of Na/PVdF/Na, and (c) 10th cycle of Na/PVdF/Na

10 mV s⁻¹ at 25 °C. The current magnitude of the SS/PVdF/SS cell is very low and there are no current peaks on the voltammogram. On the other hand, both the cathodic and anodic current peaks are present on the voltammogram of Na/PVdF/Na cell. These results suggested that the cathodic deposition and anodic oxidation of sodium are facile at Na/PVdF interface and not favored on stainless steel. From the voltammogram of Na/PVdF/Na cell, cathodic and anodic curves are very broad and current densities also decrease after the 10th cycling. The phenomenon might be related to the formation of a passivation layer.

Figure 2 shows the time dependence of the impedance data for the Na/PVdF/Na cell. The bulk resistance (R_b) of the polymer electrolyte is the intercept on the real-axis at high frequencies, which is almost constant with time. The semicircle at lower frequencies should result from the

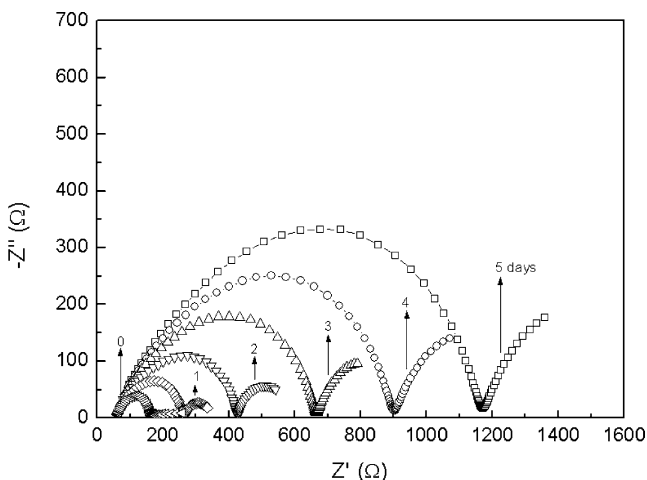


Fig. 2 Time dependence of the impedance response of Na/PVdF/Na cell at 25 °C: frequency range from 10⁵ to 0.01 Hz and Na electrode area of 0.8 cm²

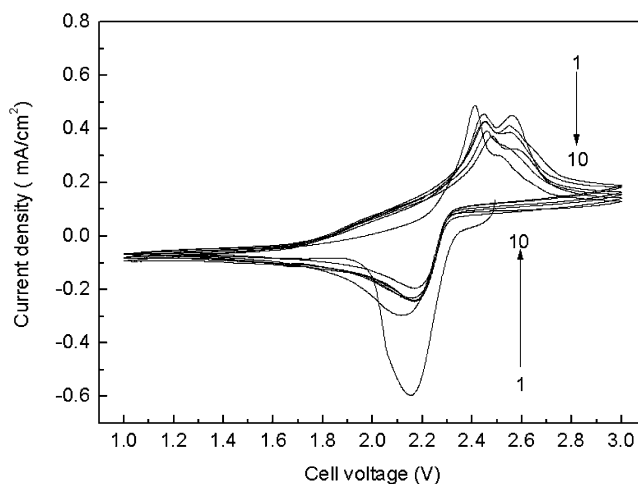


Fig. 3 Cyclic voltammograms of Na/PVdF/S cell using a scan rate of 0.1 mV s⁻¹ at 25 °C

contribution of sodium electrode/PVdF gel polymer electrolyte interface resistance. The interfacial resistance continuously increases with increasing storage time. In previous work, the interfacial resistance increased with storage time when the polymer electrolyte was in contact with metallic lithium [16]. They suggested that the interfacial resistance came from passivation layer on the electrode surface. The interfacial resistance can be associated with a passivation layer on the electrode surface which can be coincided with CV curve shown in Fig. 1.

Performance of Na/PVdF/S cells

Figure 3 shows cyclic voltammograms of Na/PVdF/S cell using a scan rate of 0.1 mV s⁻¹ at 25 °C. One large reduction peak and two oxidation peaks are observed at 2.15 V, 2.41 V, and 2.6 V, respectively. When a slow sweep rate of 0.05 mV s⁻¹ was applied to the Na/PVdF/S cell [15], two reduction (1.7 V and 2.2 V) and two oxidation peaks

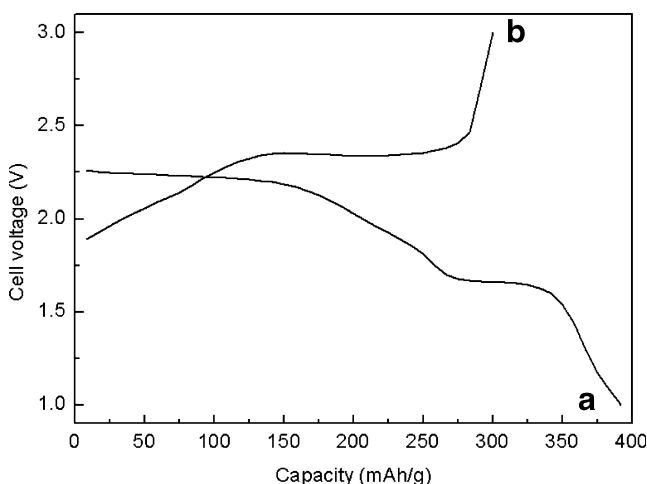


Fig. 4 First discharge curve of Na/PVdF/S cell with 0.288 mA cm⁻² at 25 °C: (a) 1st discharge and (b) 1st charge

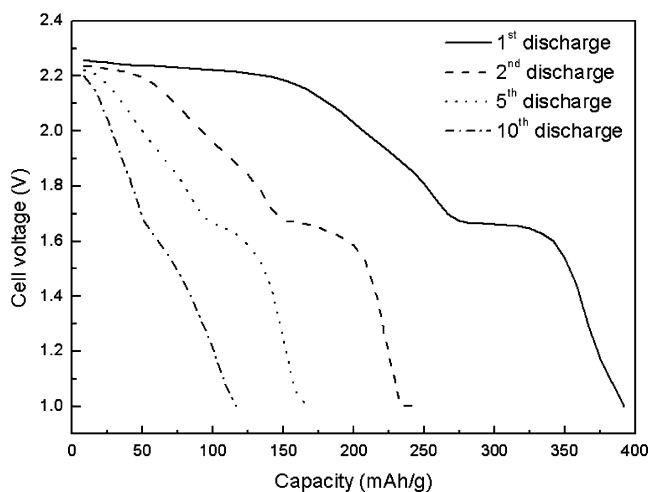


Fig. 5 Discharge curves of Na/PVdF/S cell at 25 °C with 0.288 mA cm⁻²

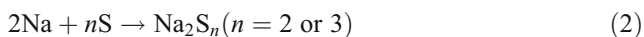
(2.1 V and 2.5 V) were observed. At a fast sweep rate of 0.1 mV s⁻¹, shown in Fig. 3, two reduction peaks are overlapped at 2.15 V and oxidation peaks shift towards higher voltages.

The cell was allowed to equilibrate under open circuit voltage (OCV) condition for 1 h before discharge reaction. Fig. 4 shows the first charge–discharge curve of the Na/PVdF/S cell at 25 °C in a constant current density of 0.288 mA cm⁻². The discharge curve shows two plateaus, which appear at 2.23 V and 1.67 V. Also, the first discharge capacity is 392 mAh g⁻¹, which is lower than the previous one in a low current density of 0.144 mA cm⁻² [15]. The first charge reaction shows a capacity of 300 mA g⁻¹, which means, an irreversible capacity of 93 mAh g⁻¹. Two potential plateaus might be related with two different reactions between sodium and sulfur, which is similar to the plateaus of the sodium/sulfur battery operated at high temperature [1]. Park et al. [12, 15] reported that the upper plateau potential at 2.23 V might be related to the formation of high polysulfides such as Na₂S_n (*n*>4) and Na₂S₂ or Na₂S₃ phases could be formed at the lower plateau of 1.67 V. They are described as follows:

Upper plateau region



Lower plateau region



Also, there are two steps during charging which might be the reverse process of discharging reaction (1) and (2). The two plateau regions during the charging process correspond to the reduction peaks in the CV curve shown in Fig. 3. Although the discharge curves show two plateau potentials, the CV curves represent only one oxidation peak. This phenomenon can be related to a rapid scan rate which induced overlapping of two reduction peaks.

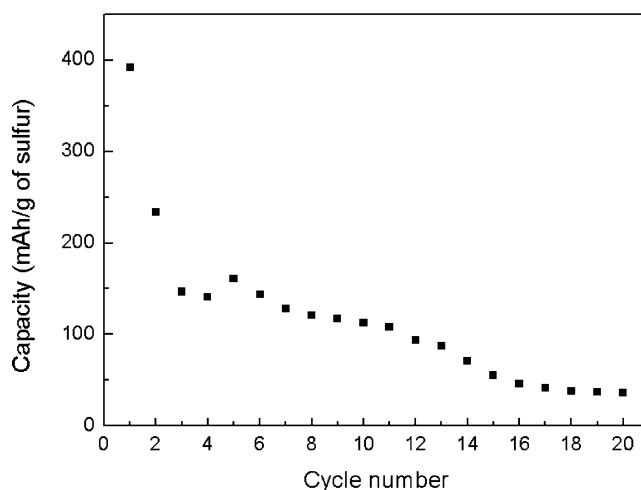


Fig. 6 Cycle performances of Na/PVdF/S cells with 0.288 mA cm⁻² at 25 °C

Figure 5 shows the changes of discharge curves for Na/PVdF/S cells as a function of the numbers of the charging–discharging cycles. The first discharge curve shows two plateau regions. The length of the plateau region decreases by repeated cycling, the upper plateau region disappears first. Also, the discharge capacity decreases continuously during cycling and becomes 117 mAh g⁻¹ after ten cycles.

Figure 6 shows the changes of discharge capacity as a function of cycle number. The capacity drastically decreases in a few cycles and gradually decreases to 36 mAh g⁻¹ after 20 cycles. Since Na/PVdF/S cell can operate at ambient temperature, it is more stable than the high-temperature Na/S cell. However, this cell shows a poor cycle life shown in Fig. 6. Recently, Wang et al. [8] reported that sodium/composite sulfur cell could improve cycling properties. They used composite sulfur with PAN and 1 M NaClO₄ EC-DMC liquid electrolyte. One of the reasons for poor cycling properties might be related to PVdF polymer electrolyte.

Conclusions

The solid-state sodium/sulfur cell employing a PVdF gel polymer electrolyte was tested at ambient temperature. The Na/PVdF/S cell shows a first discharge capacity of 392 mAh g⁻¹ in high current density of 0.288 mA cm⁻². The discharge capacity of Na/PVdF/S cell decreases continuously during cycling and becomes 36 mAh g⁻¹ after 20 cycles.

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