



Short communication

Discharge reaction mechanism of room-temperature sodium–sulfur battery with tetra ethylene glycol dimethyl ether liquid electrolyte

Hosuk Ryu^a, Taebum Kim^b, Kiwon Kim^a, Jou-Hyeon Ahn^c, Taehyun Nam^a, Guoxiu Wang^{a,d},
Hyo-Jun Ahn^{a,*}

^a School of Materials Science and Engineering, i-cube Center, PRC, WCU, ERI, Gyeongsang National University, Jinju, Republic of Korea

^b Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Osaka, Japan

^c Department of Chemical and Biological Engineering, PRC, Gyeongsang National University, Jinju, Republic of Korea

^d Department of Chemistry and Forensic Science, University of Technology, Sydney, Australia

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ABSTRACT

The first discharge curve of a sodium–sulfur cell using a tetra ethylene glycol dimethyl ether liquid electrolyte at room temperature shows two different regions: a sloping region and a plateau region of 1.66 V. The first discharge capacity is 538 mAh g⁻¹ sulfur and then decreases with repeated charge–discharge cycling to give 240 mAh g⁻¹ after ten cycles. Elemental sulfur of the cathode changes to sodium polysulfides Na₂S₂ and Na₂S₃, during full discharge. The sodium polysulfides, however, do not reduce completely to elemental sulfur after full charging. In summary, the mechanism of the battery with liquid electrolyte is $2\text{Na} + n\text{S} \rightarrow \text{Na}_2\text{S}_n (4 > n \geq 2)$ on discharge and $\text{Na}_2\text{S}_n (4 > n \geq 2) \rightarrow x(2\text{Na} + n\text{S}) + (1 - x)\text{Na}_2\text{S}_n (5 > n > 2)$ on charge.

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1. Introduction

Because of their low material cost, long cycle-life and high specific energy, sodium–sulfur (Na–S) batteries have been studied extensively for use in electric vehicles and as electric energy-storage devices [1]. Recently, Na–S batteries have become an attractive potential candidate for the storage of electricity, generated by means of renewable energy. Kummer and Weber [2] have investigated the electrochemical properties of Na–S cells above 300 °C; the cells were composed of a solid ceramic electrolyte, liquid sodium and sulfur electrodes. One severe problem of the Na–S battery was that high operating temperatures, i.e., above 300 °C, could induce explosion, corrosion and power consumption by heating. Recently, Park [3,4] and Kim et al. [5] reported on a lower temperature Na–S battery using a polyethylene oxide (PEO) and polyvinylidene fluoride (PVdF) polymer electrolyte. The PEO and PVdF polymer electrolyte has a lower ionic conductivity than that of liquid electrolytes at room temperature. Liquid electrolytes such as ethylene carbonate (EC)/dimethyl carbonate (DMC), propylene carbonate (PC) and EC/PC, with high ionic conductivity, have been used for sodium-ion batteries [6–9]. There have, however, been few studies of sulfur electrodes for sodium batteries with liq-

uid electrolytes, although it is thought that such electrodes could yield good ionic conductivity. Wang et al. [10] investigated a sulfur composite cathode for sodium batteries with a EC/DMC liquid electrolyte. A glyme system of electrolytes such as tetra ethylene glycol dimethylether (TEGDME) has often been used as the sulfur electrode for lithium batteries [11]. There have been no studies of the electrochemical properties and charge–discharge mechanism of a room-temperature Na–S battery with a liquid electrolyte.

In this study, the electrochemical properties of a Na–S battery with a TEGDME electrolyte are investigated. The mechanism of the charge–discharge reaction is examined by means of X-ray diffraction (XRD) analysis, differential scanning calorimetry and charge–discharge curves.

2. Experimental

All raw materials were pretreated before use. Sulfur (<50 μm) was sieved to –300 mesh (<25 μm) and then dried at 80 °C for 24 h. Carbon and PEO were dried under vacuum for 24 h at 90 and 50 °C, respectively. The sulfur electrode was prepared from a suspension of 60 wt.% elemental sulfur powder, 20 wt.% carbon and 20 wt.% PEO in acetonitrile (ACN). The suspension was mixed for 24 h by stirring. The suspension was consecutively mixed for 2 h by ball-milling and then cast on an aluminum current-collector. The sulfur electrode film was made after drying at room temperature for 24 h. In order to remove impurities and moisture, the sulfur electrode

* Corresponding author.

E-mail address: ahj@gnu.ac.kr (H.-J. Ahn).

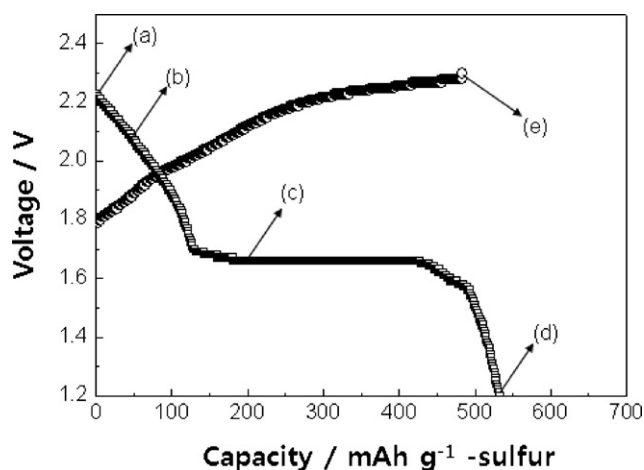


Fig. 1. First discharge-charge curves of Na-S battery with liquid electrolyte at room temperature and analysis points of sulfur electrode such as (a) original sulfur electrode, (b) discharged to 50 mAh g^{-1} sulfur in sloping region, (c) discharged to 200 mAh g^{-1} sulfur in plateau region, (d) fully discharged to 1.2 V, and (e) fully charged to 2.3 V.

film was dried continuously at 30°C for 24 h under vacuum. The sulfur cathode was prepared by punching the sulfur electrode film into a circular disc. The anode was prepared by cutting it from a sodium ingot and then punching it to the same size as that of the cathode. All of the preparation process was carried out in a glove-box filled with argon gas. The liquid electrolyte was prepared by dissolving 1 M NaCF_3SO_3 in TEGDME by stirring for 24 h. Sodium trifluoromethane-sulfonate (NaCF_3SO_3) was dried under vacuum at 100°C for 24 h. TEGDME was treated using a 4 Å molecular sieve for 72 h; the sample had less than 20 ppm of moisture according to measurement with a Karl Fischer coulometer (Metrohm). The ionic conductivity of the electrolyte was determined from the AC impedance spectrum of a blocking cell, which was assembled by placing the electrolyte between two stainless-steel electrodes. The data were collected over a frequency range of 10 mHz to 100 kHz. The specific ionic conductivity of the 1 M NaCF_3SO_3 -TEGDME liquid electrolyte for the Na-S battery is $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , i.e., higher than that of the PVdF gel electrolyte using TEGDME.

The Na-S cell was assembled by stacking, in turn, a sulfur cathode, a porous polypropylene separator (Celgard 2200) with liquid electrolyte and a sodium anode in a Swagelok type cell. The cell was charged and discharged at room temperature (25°C) with a constant specific current density of 0.144 mA cm^{-2} after a rest time of 1 h. The cut-off voltage for charge and discharge was 2.3 and 1.2 V, respectively. The crystal structure of the sample was investigated by means of XRD analysis. Scanning electron microscopy (SEM) was used to observe changes in the surface morphology of the electrodes. Elemental analysis was performed by energy dispersive X-ray spectroscopy (EDS). The thermal stability of the sulfur electrode was investigated with differential scanning calorimetry (DSC).

3. Results and discussion

The first discharge-charge curves of an Na/TEGDME/S cell at room temperature are given in Fig. 1. The Na/TEGDME/S cell shows a discharge capacity of 538 mAh g^{-1} , which is similar to that of a cell using a polymer electrolyte [3–5]. Also, the capacity is higher than that reported for sodium ion batteries at room temperature [6–9]. The discharge process using a TEGDME-based electrolyte can be divided into two regions: a sloping region in the range of 2.23–1.66 V, and a plateau region at 1.66 V. The overall discharge profile for the Na-S cell with the TEGDME-based electrolyte is sim-

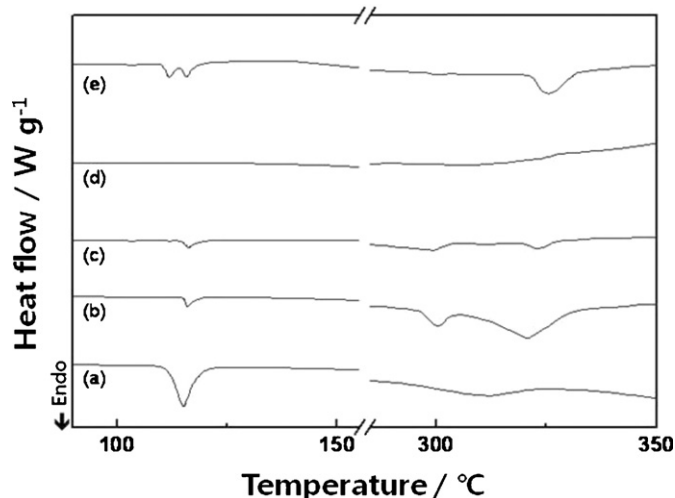


Fig. 2. DSC curves of sulfur electrode with various cut-off voltage conditions such as (a) original sulfur electrode, (b) discharged to 50 mAh g^{-1} sulfur in sloping region, (c) discharged to 200 mAh g^{-1} sulfur in plateau region, (d) fully discharged to 1.2 V, and (e) fully charged to 2.3 V.

ilar to that found previously using PEO [3] and PVdF [4,5] polymer electrolytes, which had two plateau regions at 2.3 and 1.7 V. The discharge curves of a battery using TEGDME liquid electrolyte do not show a first plateau at 2.3 V. The discharge profile of an Na-S battery with an EC/DMC liquid electrolyte [10] is different.

In order to investigate the discharge-charge reaction mechanism, the Na-S cell was cut off at the indicated points and the sulfur electrode was investigated at the points shown in Fig. 1, such as the original sulfur electrode (a), discharged to 50 mAh g^{-1} sulfur in the sloping region (b), discharged to 200 mAh g^{-1} sulfur in the plateau region (c), fully discharged to 1.2 V (d), and fully charged to 2.3 V (e).

The DSC curves of the sulfur electrode at each marked point during the discharge-charge process are presented in Fig. 2. The original sulfur electrode (a) in Fig. 2 has an endothermic peak of 114°C , which came from elemental sulfur, as previously reported [11]. During the discharge reaction, the area of the peak at 114°C continuously decreases and new endothermic peaks appear at 303 and 321°C . From the Na_2S -S phase diagram [1], the melting points of Na_2S , Na_2S_2 , Na_2S_3 , Na_2S_4 and Na_2S_5 are 1176 , 475 , 235 , 285 and 258°C , respectively. The new peaks at 303 and 321°C may be related to sodium polysulfides such as Na_2S_4 and Na_2S_5 . The amount of elemental sulfur decreases, and sodium polysulfides such as Na_2S_4 and Na_2S_5 are formed during discharge. In the fully-discharged sample (Fig. 2(d)), there is no evidence of endothermic peaks, which indicates a total lack of elemental sulfur or sodium polysulfides such as Na_2S_4 and Na_2S_5 in the sulfur electrode. For the fully-charged sample (Fig. 2(e)), small endothermic peaks appear at 113 and 118°C and can be explained by the recovery of elemental sulfur. Also, as the fully-charged reaction proceeds (e), a peak appears at 323°C . Elemental sulfur and sodium polysulfide such as Na_2S_4 and Na_2S_5 may exist in the fully-charged sulfur electrode. For analysis of the material at the high temperature peaks (300 and 320°C) in the DSC curve, the reaction products at each point were investigated by means of XRD.

The changes in the X-ray diffraction patterns of sulfur electrodes as a function of the discharge-charge process are shown in Fig. 3. The original sulfur electrode has an orthorhombic structure, which matches the structure of elemental sulfur. The peak intensity of elemental sulfur decreases during the discharge process, and finally disappears at full discharge. In the initial sloping stage of the discharge process (b), various new peaks appear and can be indexed

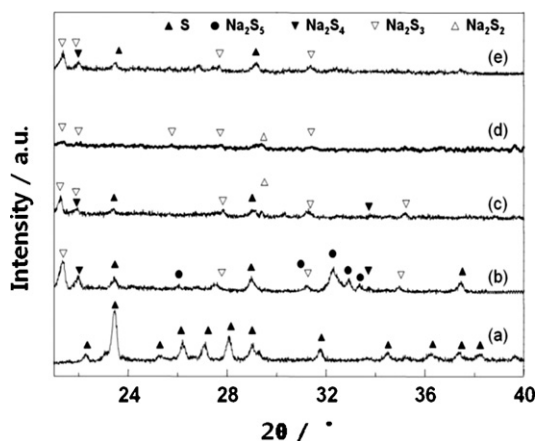


Fig. 3. XRD patterns of sulfur electrode with various cut-off voltage conditions such as (a) original sulfur electrode, (b) discharged to 50 mAh g⁻¹ sulfur in sloping region, (c) discharged to 200 mAh g⁻¹ sulfur in plateau region, (d) fully discharged to 1.2 V, and (e) fully charged to 2.3 V.

as Na₂S₂, Na₂S₃, Na₂S₄ and Na₂S₅. The peaks of Na₂S₅ disappear in the plateau region of discharge (c). For the fully-discharged sample (Fig. 3(d)), only Na₂S₃ and Na₂S₄ peaks are observed. Na₂S is not detected in the fully-discharged sample. From the X-ray diffraction results, the following reactions can be suggested.

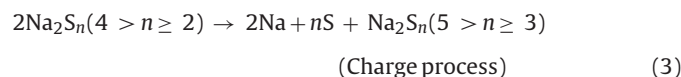
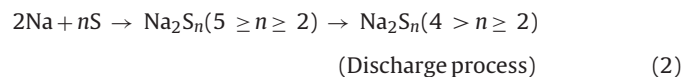


In the XRD and DSC results, sulfur of the cathode partly changes into Na₂S₅, Na₂S₄, and Na₂S₃ in the initial sloping stage of the discharge process (b). An XRD peak is detected but a DSC peak for Na₂S₃, is not detected because of the low melting temperature (235 °C). Sulfur and all of the polysulfides such as Na₂S_n (2 < n ≤ 5) exist in the plateau region (1.66 V) of the sulfur electrode with the discharge of 200 mAh g⁻¹ sulfur (c). As the amount of Na₂S₅ is very small, it is detected in the DSC results but not in the XRD results. Also, the sulfur of the cathode changes into Na₂S₃ and Na₂S₂ during the full discharge process (d). An XRD peak for Na₂S₃ is found, but no DSC peak is observed because of the high melting temperature (476 °C).

Table 1
EDS results of sulfur electrode with various cut-off voltage conditions.

Sample	Elements	
	Na (at.%)	S (at.%)
(a) Original sulfur electrode	0.0	100.0
(b) 1 h discharge	24.0	76.0
(c) 4 h discharge	36.7	63.3
(d) Full discharge	46.9	53.1
(e) Full charge	26.4	73.6

In the XRD and DSC results, elemental sulfur changes to sodium polysulfides during the discharge and charge processes, according to the following reactions.



Nevertheless, with the formation of Na₂S₂, as well as of Na₂S₃, from the results of XRD and DSC, the capacity of room-temperature Na–S batteries with TEGDME should be lower than 538 mAh g⁻¹ sulfur based on the formation of Na₂S₃; this value is the theoretical capacity of a Na–S cell at high temperature (over 300 °C).

An investigation was made of the surfaces of the electrodes by means of SEM and ESD in order to determine the reaction in the electrode. The SEM morphologies of the sulfur electrode during the discharge–charge process are given in Fig. 4. The original sulfur electrode consists of a homogenous mixing of powders such as sulfur, carbon and binder material. The surface of the electrode during discharge (Fig. 4(b) and (c)) is covered with materials that are products of the reactants, such as lithium and sulfur, and bunched small particles, which are related to agglomerates of the components. In the fully-discharged sulfur electrode, the material wholly covers the surface of the sulfur electrode. The shape of the fully-charged electrode surface does not, however, return to its shape before discharge, and has larger size particles than those shown in Fig. 5(a).

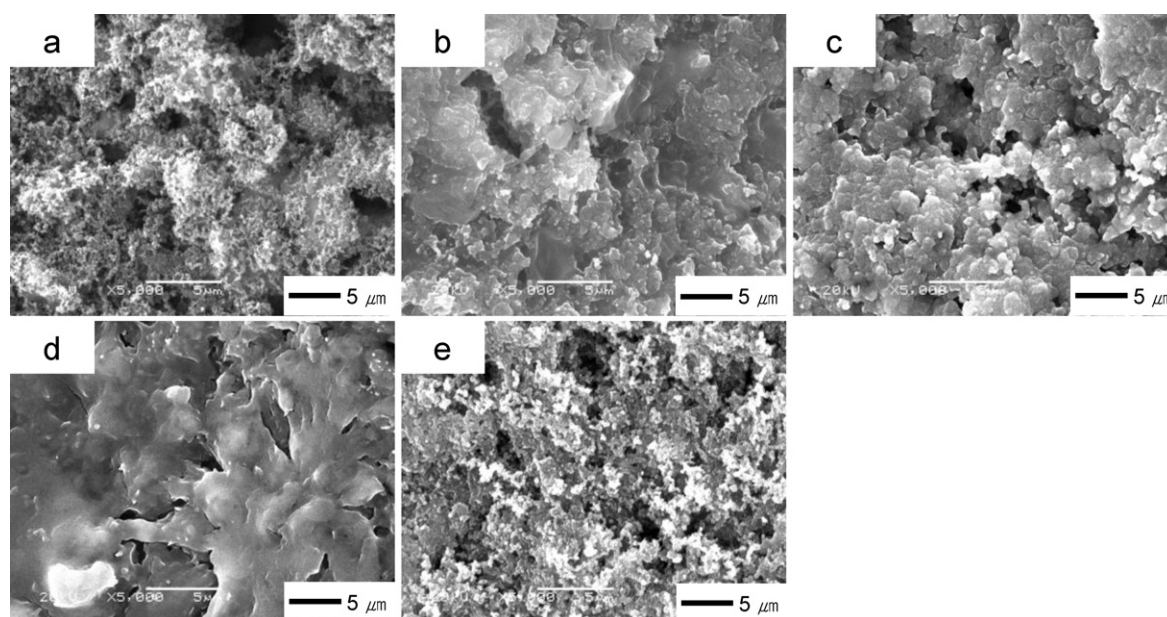


Fig. 4. SEM photographs of sulfur electrode with various cut-off voltage conditions such as (a) original sulfur electrode, (b) discharged to 50 mAh g⁻¹ sulfur in sloping region, (c) discharged to 200 mAh g⁻¹ sulfur in plateau region, (d) fully discharged to 1.2 V, and (e) fully charged to 2.3 V.

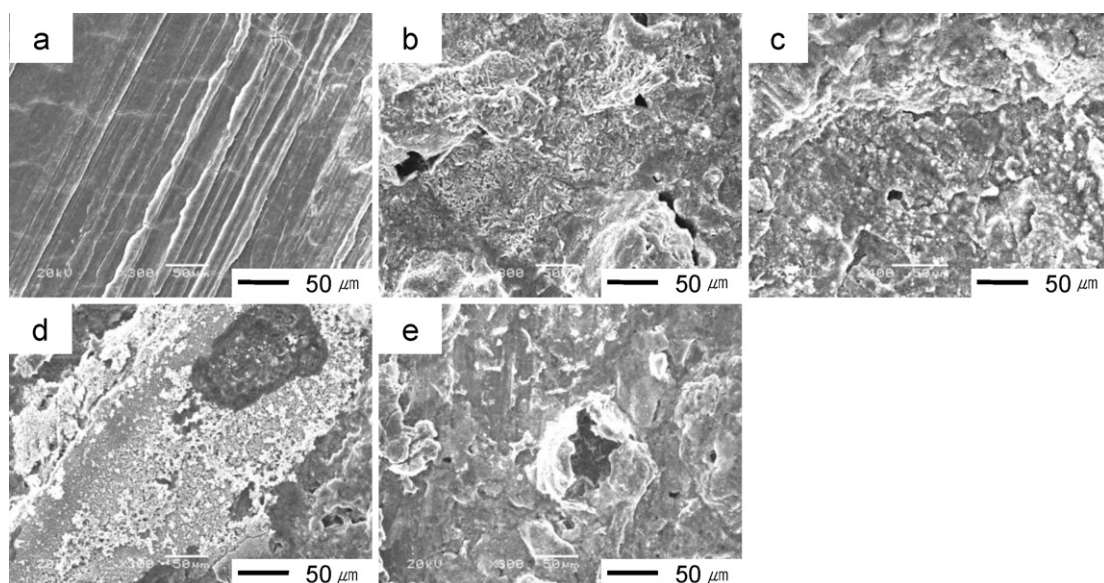


Fig. 5. SEM photographs of sodium electrode with various cut-off voltage conditions such as (a) original sulfur electrode, (b) discharged to 50 mAh g^{-1} sulfur in sloping region, (c) discharged to 200 mAh g^{-1} sulfur in plateau region, (d) fully discharged to 1.2 V, and (e) fully charged to 2.3 V.

Table 1 lists the EDS results for the sulfur electrode as a function of the discharge–charge process. During the discharge process, the content of sodium increases in the sulfur electrode because the elemental sulfur in the sulfur electrode reduces continuously to sodium polysulfides. The ratio of sulfur to sodium is about 53:47 in the fully-discharged sulfur electrode (d). Therefore, the final product might be Na_2S_2 , which is different from the product shown in the XRD and DSC results. The increase in the Na ratio in EDS is a result of the sodium salt in the electrode due to the electrolyte. Sodium exists in the fully-charged cathode (e); therefore, sodium does not return completely to the anode. The SEM images of the sodium anode during the discharge–charge process are given in Fig. 5. The original sodium electrode (Fig. 5(a)) has a smooth surface after cutting. During discharge (Fig. 5(b)–(d)), the surface is partly covered with materials that are the products of the reactants (sodium and sulfur) or oxide materials of these products because of the ex situ analysis and high reactivity of the product. The surface of the sodium electrode after full charging (Fig. 5(e)) remains covered with materials as a thin film that is formed by the reaction between the sodium (anode), products and/or oxygen.

Table 2 shows EDS of the sodium electrode as a function of the discharge–charge process for investigation of the moving sulfur ratio in the sodium anode. The content of sulfur in the anode increases with the discharge progress. Sulfur on the cathode moves to the sodium anode through the electrolyte during discharge. This phenomenon can be explained by the dissolution of sulfur or sodium polysulfides into the liquid electrolyte. The final discharge products of Na_2S_3 and Na_2S_2 are shown in the XRD results (Fig. 3). The first discharge capacity of 532 mAh g^{-1} sulfur is lower than the

Table 2
EDS results of sodium electrode with various cut-off voltage conditions.

Sample	Elements	
	Na (at.%)	S (at.%)
(a) Original sodium electrode	100.0	0.0
(b) 1 h discharge	90.9	9.1
(c) 4 h discharge	61.6	38.4
(d) Full discharge	42.7	57.3
(e) Full charge	65.1	34.9

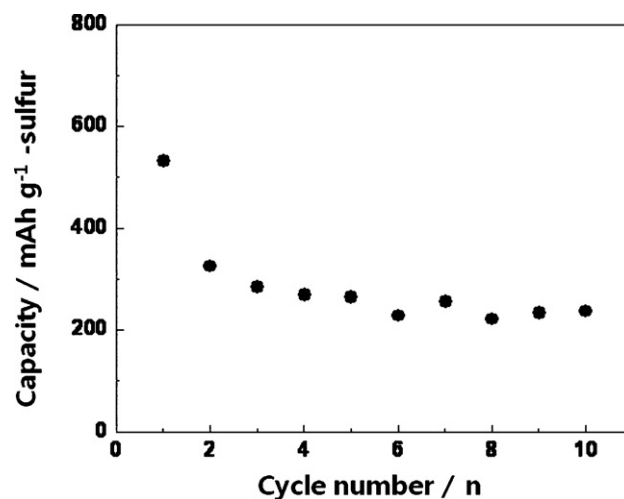


Fig. 6. Cycle characteristics of Na–S battery with liquid electrolyte at room temperature.

theoretical specific capacities of Na_2S_3 and Na_2S_2 , which can be calculated at 558 and 837 mAh g^{-1} sulfur, respectively. This lower capacity is explained by the fact that the products of the reactant, such as sodium and sulfur, are dissolved in the electrolyte, as seen in the results of SEM and EDS.

The cyclical characteristic of the Na–S battery at room temperature is shown in Fig. 6. The discharge capacity directly decreases from 538 to 316 mAh g^{-1} during the second cycle. The battery is kept at a discharge capacity between 230 and 300 mAh g^{-1} after the second cycle. In Fig. 6, the discharge capacity of the Na–S cell can be seen to show a sharp decline over the two cycles; finally, the capacity fade rate diminishes substantially. This decrease indicates that the fully-charged sulfur electrode does not perfectly recover to elemental sulfur and exists as polysulfides such as Na_2S_4 , Na_2S_3 and Na_2S_2 , as shown in DSC (Fig. 2(e)) and in the XRD results (Fig. 3(e)); sulfur on the anode after full charging does not move to the cathode, as can be seen in the results of EDS (Table 2).

The discharge capacity remained at 238 mAh g^{-1} after ten cycles, which is a much shorter cycle-life than that of high temperature (over 300°C) Na–S batteries.

4. Conclusions

A liquid electrolyte of TEGDME and NaCF_3SO_3 salt has a sodium ionic conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C and can be used for a Na–S battery at room temperature. The discharge curve has two regions: a sloping region between 2.23 and 1.66 V and a plateau region of 1.66 V. A Na–S cell using liquid electrolyte shows a first discharge capacity of 538 mAh g^{-1} at room temperature, which is lower than that of high temperature Na–S cells. The discharge capacity remains at about 250 mAh g^{-1} to the 10th cycle after sharply decreasing in the second cycle. From XRD, DSC and EDS results, the final discharge products are Na_2S_3 and Na_2S_2 . The decrease in discharge capacity is due to a decrease in active material by dissolution of sulfur or sodium polysulfides into the electrolyte and the irreversible reduction from sodium sulfides to elemental sulfur at full charge.

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