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Dependence of $LiNO_3$ decomposition on cathode binders in Li–S batteries

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HIGHLIGHTS

- Interactions between cathode binders with modified electrolytes in LSBs.
- How oxygen-functional groups influence the decomposition of $LiNO_3$.
- Comparison among alginate, CMC and PVDF binders.
- Alginate and CMC: decomposition of $LiNO_3$ enhanced at potentials <1.8 V.
- Rational choice of the binders used in sulfur composite cathodes.

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ABSTRACT

This study brings a new insight into the interfacial compatibility of cathode binders with modified electrolytes in lithium–sulfur batteries. We compared the oxygen-containing binders sodium alginate (NaAlg) and sodium carboxymethyl cellulose (NaCMC) with the conventional oxygen-free polyvinylidene difluoride. The results revealed that the NaAlg and NaCMC binders strongly facilitated the decomposition of the electrolyte additive $LiNO_3$ at potentials lower than 1.8 V. This is primarily attributed to the influence of oxygen-containing functional groups. However, when $LiNO_3$ was absent from the electrolyte, the sulfur cathode with the NaAlg binder showed the most stable performance. To prevent $LiNO_3$ decomposition and acquire stable cycling, the discharge voltage was limited to 1.8 V. At the conclusion of testing (100 cycles, voltage cutoff = 1.8 V), the NaAlg-based cathode maintained 608 mAh g^{-1} of capacity (52% of the initial capacity). This represented a 35% increase in the specific capacity obtained at the 100th discharge cycle with the cutoff voltage at 1.5 V. Our results suggest a rational choice of the binders used in sulfur composite cathodes.

1. Introduction

In recent years lithium–sulfur batteries (LSBs) have created great interest in the electrochemistry community because of their highly promising features. Sulfur cathodes can undergo a quasi-reversible reduction to Li_2S with a theoretical specific capacity of 1675 mA h g^{-1}, which is almost three times the capacity provided by the current intercalation cathodes. However, the complexity of the capacity fading mechanism of LSBs has been a technical barrier to their practical use. The redox chemistry of sulfur in the cathode relies on a solid (cyclo-S_8)–liquid (chain polysulfides (PS, S^{2-}_{4-8}))–solid (Li_2S_2/Li_2S) reaction with a systematic decrease in the ion chain length [1]. The reactions between the insoluble Li_2S_2/Li_2S deposits on the Li anode with PS ions in solution give rise to medium-chain ions, which can diffuse back to the sulfur cathode. This process is called the "PS shuttle mechanism" which is characterized by: (1) active mass loss from the cathode, (2) reduction of coulombic efficiency, and (3) capacity decay upon cycling [1].

Additives in the electrolyte solution are an effective way to avoid the PS shuttle [2]. Lithium nitrate ($LiNO_3$) is the most-used additive

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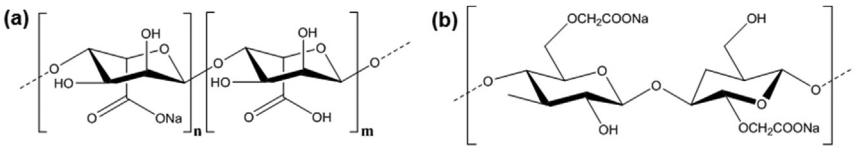

Fig. 1. Molecular structures of (a) sodium alginate and (b) sodium carboxymethyl cellulose.

in electrolyte solutions of LSBs. According to Zhang [3], $LiNO_3$ plays different roles at the anode and cathode. At the anode, the $LiNO_3$ leads to formation of a stable passivation film which limits the PS shuttle. However, with the progressive consumption of $LiNO_3$ during cycling, the passivation film grows endlessly causing capacity fading. On the cathode surface at potentials lower than 1.6 V, $LiNO_3$ may be reduced irreversibly [3–5].

Although several papers [2,5–7] have reported the use of $LiNO_3$ in the electrolyte, no information has been given regarding the effects of the binder's functional groups on $LiNO_3$ decomposition under low potential values (<1.6 V). Currently, poly(vinylidene difluoride) (PVDF) has been widely used as the binder for both the negative and positive electrodes in lithium ion batteries (LIBs), due to its good electrochemical stability and high adhesion to electrode materials and current collectors. However, there is increasing interest in finding cheaper and environmentally friendly binders, such as sodium alginate (NaAlg) and sodium carboxymethyl cellulose (NaCMC), to replace the current PVDF binder [8–10].

The combination of active sulfur and conductive carbon is very important for a high performance sulfur cathode. A suitable binder for sulfur cathode preparation may represent a powerful component in improving the cathode performance. A high performance binder should have high adhesion ability for the electrode materials to the current collector, as well as the ability to form a good electric network between the active material and conductive carbon, to facilitate electron transport as well as the diffusion of lithium ions [10–12].

This paper presents new insights into $LiNO_3$ decomposition in the presence of NaAlg and NaCMC based cathodes. NaAlg is produced from brown seaweed by the use of dilute alkali. It consists mainly of the sodium salt of alginic acid, a polysaccharide composed of β-D-mannuronic acid (M) and a-L-guluronic acid (G). The relative amount and sequential distribution of homogeneous M–M segments (M-blocks), homogeneous G–G segments (G-blocks), and alternating M–G segments (MG-blocks), which represent the primary structure of NaAlg, depend on the producing species, and for marine sources, on seasonal and geographical variations [13]. NaCMC is a chemical derivative of cellulose where some of the hydroxyl groups (–OH) are substituted with carboxymethyl groups ($-CH_2COOH$). The properties of NaCMC depend on the degree of substitution and the length of the cellulose chains. The abundance of oxygen functional groups in the NaAlg and NaCMC binders (Fig. 1) may result in a chemical influence on the cathode behavior. This work shows that the oxygen-containing binders can strongly promote the $LiNO_3$ decomposition.

2. Experimental

2.1. Materials

Carbon black was commercially purchased. The electrolyte 1 M bis(trifluoromethane) sulfonimide lithium (LiTFSI) salt in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 vol) was used as ordered without further purification. Sulfur, sodium alginate and sodium carboxymethyl cellulose were used as purchased from Sigma–Aldrich.

2.2. Carbon–sulfur active material preparation

The carbon–sulfur active material was prepared by stirring 6 mL of carbon disulfide with carbon black (200 mg) and sulfur (120 mg) for approximately 2 h at room temperature (until solvent evaporation). The remaining sample was dried in an autoclave oven at 160 °C overnight. All the prepared carbon–sulfur composites had 40 ± 1 wt% of sulfur according to thermogravimetric analysis (data not shown).

2.3. Cathode preparation

The cathodes were made from 80 wt% active composite (C–S), 10 wt% carbon black (conducting agent) and 10 wt% binder. Three types of binders were tested: NaAlg, NaCMC and PVDF. The cathode was prepared as a slurry with the solvent listed in Table 1 and then was blade-cast onto aluminum foil.

2.4. Battery assembly and performance evaluation

Coin-type cells were assembled in an Ar-filled glove box (MBraun Unilab). Lithium metal foil was used as anode, and the carbon–sulfur composite on aluminum foil as cathode. The electrolyte was composed of a 1 mol L^{-1} lithium bis-trifluorometha nesulfonylimide (LiTFSI) solution in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume) with/without $LiNO_3$ (0.1 mol L^{-1}) as additive (Table 1).

The coin-cell performance was evaluated by using a LAND instrument. The current density (CD) was set to 1675 mA g^{-1} (1C) for cell testing, referred to the mass of sulfur in the cathode. The charge–discharge voltage range was 1.5 V–2.8 V vs. Li^+/Li^0. All of the specific capacities were calculated based on the mass of sulfur (40 ± 1 wt%).

Table 1
Nomenclature regarding to cathode preparation and battery assembly.

Nomenclature	Cathode preparation		Battery assembly
	Binder (10%)	Solvent (slurry formation)	Additive [$LiNO_3$] = 0.1 mol L^{-1}
NaAlg-S(0.4)-$LiNO_3$(0.1 M)	SA	Aqueous	Yes
NaAlg-S(0.4)-$LiNO_3$(0)	SA	Aqueous	No
NaCMC-S(0.4)-$LiNO_3$(0.1 M)	CMC	Aqueous	Yes
NaCMC-S(0.4)-$LiNO_3$(0)	CMC	Aqueous	No
PVDF-S(0.4)-$LiNO_3$(0.1 M)	PVDF	N-methyl pyrrolidinone (NMP)	Yes
PVDF-S(0.4)-$LiNO_3$(0)	PVDF	N-methyl pyrrolidinone (NMP)	No