

Short communication

Correlation between positive-electrode morphology and sulfur utilization in lithium–sulfur battery

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Abstract

Lithium–sulfur batteries using positive electrodes (cathodes) with various binders are assembled to examine the correlation between cathode morphology and battery performance. The pore distribution and pore area of the cathodes are measured and to understand the effect on sulfur utilization on the discharge rate. The matrix of binders consists of polytetrafluoroethylene (PTFE) + carboxymethyl cellulose (CMC), PTFE + polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP). The cathode with PTFE + CMC (18:2 wt.%) as binder shows the greatest enhancement of capacity. The specific surface area of the composite material and the sulfur utilization in this cathode are about $10 \text{ m}^2 \text{ g}^{-1}$ and more than 65%, respectively.

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1. Introduction

Lithium-ion batteries and lithium–polymer batteries have been the subject of intense research and development over the past 10 years due to their advantages of high specific energy, high operating voltage, and low self-discharge rate. It is still necessary, however, to enhance the capacity of the positive electrode (cathode) in order to meet the performance needs of new energy devices that require high capacity. The limitation of the extent of lithium intercalation into transition metal oxides is the factor that has stimulated research of lithium–sulfur rechargeable batteries.

Lithium–sulfur batteries consist of a composite positive electrode (cathode), a polymer or a liquid electrolyte, and a lithium negative electrode (anode). The composite cathode is made from elemental sulfur, carbon black, and binder. A battery based on the lithium–elemental-sulfur redox couple has a theoretical specific capacity of 1675 mAh g^{-1} based on active material, on the assumption of the complete reaction of lithium with sulfur to Li_2S [1]. Although the lithium–sulfur battery has many advantages, it is impossible to discharge fully a battery with a such a cathode because sulfur is

known to be insulator. A practical lithium–sulfur battery must therefore incorporate well-distributed electrically conducting and lithium-ion conducting phases in the cathode [1,2].

Polymer electrolytes may play an important role in the performance of lithium batteries and much effort has been focused on the improvement of the polymer electrolyte in terms of the ionic conductivity and the mechanical properties. Chu [2] has shown that all-solid lithium–sulfur cells have a high capacity value for a single discharge at high temperature. Poly(ethylene oxide) (PEO) as a polymer electrolyte or as a binder in the cathode unfortunately presents some problems, such as poor mechanical properties and low ionic conductivity at low temperature [3].

Prior studies of lithium–sulfur cells with liquid electrolytes have revealed the serious problems of low active-material utilization due to the insulating nature of sulfur and Li_2S . Also, degradation of the lithium electrode in liquid organic electrolytes has limited the performance of such cells [4–7].

This work examines the relationship between morphology and sulfur utilization in a lithium–sulfur battery with liquid electrolyte. The pore distribution of cathodes with various polymers as binder, as well as the interfacial properties between the sulfur electrode and liquid electrolyte, has been investigated.

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2. Experimental

2.1. Preparation of cathode

Sulfur (99.98%, Aldrich) and Super-P carbon (MMM carbon) as a conducting agent were dried at 60 and 120 °C for 24 h under vacuum, respectively. Carboxymethyl cellulose (CMC, WS-C, DAI-ICHIKOGYO SEIYAKU), polyvinyl alcohol (PVA, 220E, Kureha), polyvinylpyrrolidone (PVP, Fluka), and polytetrafluoroethylene (PTFE) emulsion (ADI, ASAHI Glass) were used as binders in the cathode. A mixture of sulfur and Super-P was mixed with heavy duty blender (Dynamics Corporation) for 30 s at a high level. This procedure was repeated five times, and then the binder solution was added to the mixture. Distilled water and ethyl alcohol (95:5, by volume) was used as a binder solution for mixtures of PTFE–CMC and PTFE–PVA, and dimethylformamide (DMF) was used for PVP. After mixing in a ball-mill for 48 h, the cathode slurry was cast on both faces of an aluminum foil with a thickness of 15 μm and dried under vacuum at 60 °C until the solvent was evaporated completely (Table 1). The cathode was cut into 2.1 cm \times 21 cm pieces and dried for 24 h under vacuum at 60 °C again. The loading amount of sulfur was about 1.05 mg cm⁻².

Table 1
Composition of cathodes

Cathode	Composition (wt.%)			Mean pore diameter (μm)
	Sulfur	Carbon black	Binder	
1	52	28	PVP (MW 3.6×10^5) 20	23.29
2	59	31	PVP (MW 3.6×10^5) 10	19.45
3	52	28	PVP (MW 5.5×10^3) 20	21.55
4	52	28	PTFE + PVA (10:10) 20	12.50
5	52	28	PTFE + CMC (18:2) 20	19.61

2.2. Preparation of electrolyte

Dimethoxy ethane (DME) was obtained from Aldrich, and sulfolane and 1,3-dioxolane (DOL) from Fluka. Before use, the solvents were purified with molecular sieve 5 Å. Lithium bis(trifluoroethansulfone) imide (LiTFSI, Fluka) was used as a lithium salt after drying at 120 °C for 12 h under vacuum. The composition of the electrolyte was 1 M LiTFSI in DME:sulfolane:DOL (3:1:1 by volume).

2.3. Examination of cathode morphology

The cathode coated on the aluminum foil was used for measurement of pore distribution and pore area. A Micromeritics mercury porosimeter (Autopore IV 9500) was used to analyze the cathode structure. The mercury filling pressure applied to the cathode was varied from about 22 to 3.095×10^5 mm Hg after the cathode was evacuated for 5 min. The equilibration time was 10 s. The range of mean pore diameter was measured between about 400 and 0.01 μm .

The composite powder was separated from the aluminum foil in the cathode and then subjected to measurement of specific surface area (SSA). The SSA was measured by the BET method using a Quantachrome Autosorb Automated Gas Adsorption System.

2.4. Battery assemble and testing

All batteries were assembled in a dry room in order to minimize the troublesome effect of ambient water. The dew point in the dry room was kept below -50 °C. Each lithium–sulfur battery was constructed by winding together a sulfur cathode, a separator (ENTEK #F23), and a lithium-metal foil with a thickness of 100 μm . About 0.5 g of 1 M LiTFSI in DME/sulfolane/DOL as electrolyte was introduced. Battery performance was evaluated with a battery cyler (Toyo TOSCAT-3000U).

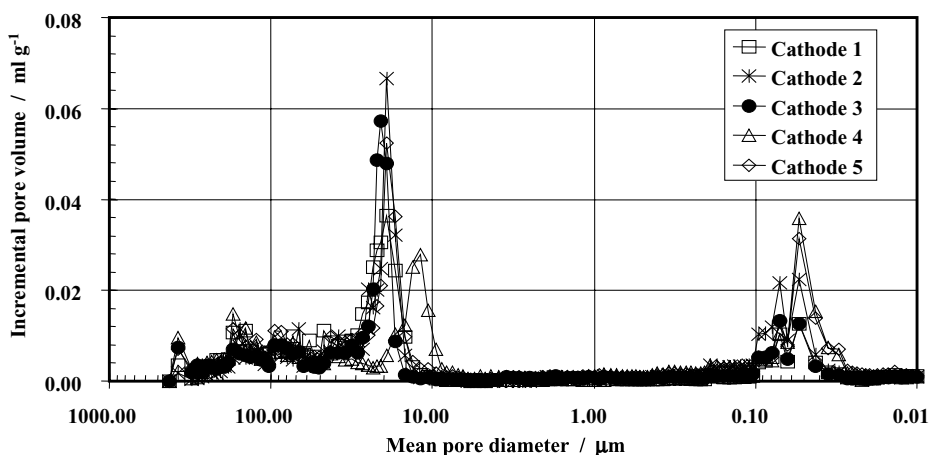


Fig. 1. Pore distribution in cathodes with various binders.

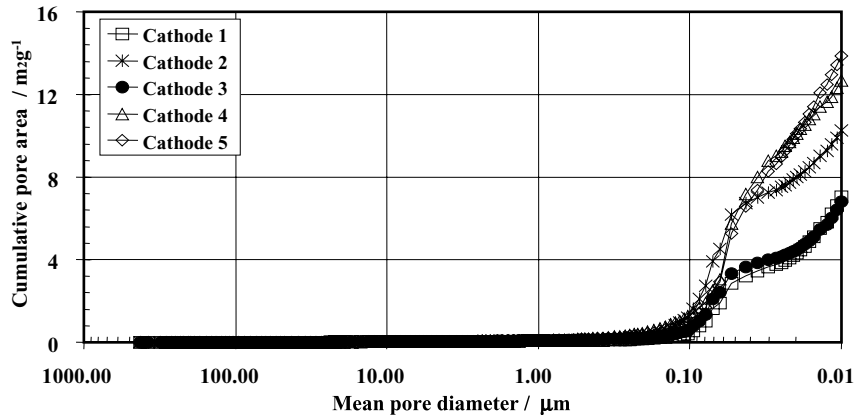


Fig. 2. Cumulative pore area with different pore size in cathodes.

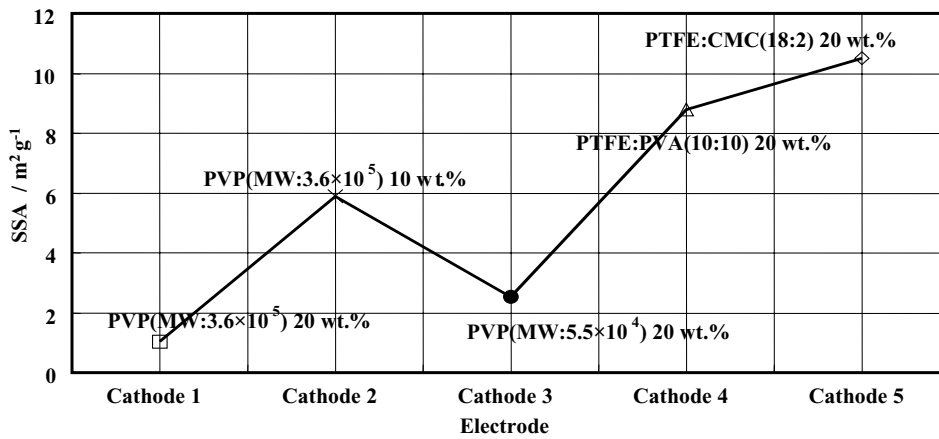


Fig. 3. Specific surface area of cathode composite material with various binders.

3. Results and discussion

The pore distributions within cathodes with various binders are shown in Fig. 1. Peaks are observed around pores with an average diameter of about 20 and 0.05 μm , respectively. This means that the pore distribution is independent of the type of binder that has been introduced into the cathode. Rather, it varies with the physical properties of the elemental sulfur and the carbon black that have been mixed in the cathode. For the same range, the cumulative pore area with different pore size is given in Fig. 2. Pores with diameters less than about 0.05 μm have the greatest effect the total pore area of the cathode; larger pores have a negligible effect. These observations are especially true for cathodes that use PTFE as a binder. The results may indicate that insoluble small particles of PTFE in the emulsion phase cause the development of pores with large area within the cathode.

It is found that the surface area of cathodes with PTFE is relatively high compared with that of PTFE-free cathodes, see Fig. 3. In the case of cathode composite material made from PVP only, the higher the molecular weight and the mixed content, the greater the surface area. The SSA of the

cathode with PTFE+CMC (18:2) is higher than that of other cathodes. It is thought that the introduction of PTFE into the cathode can increase the SSA due to the development of small pores (diameter 0.05 μm).

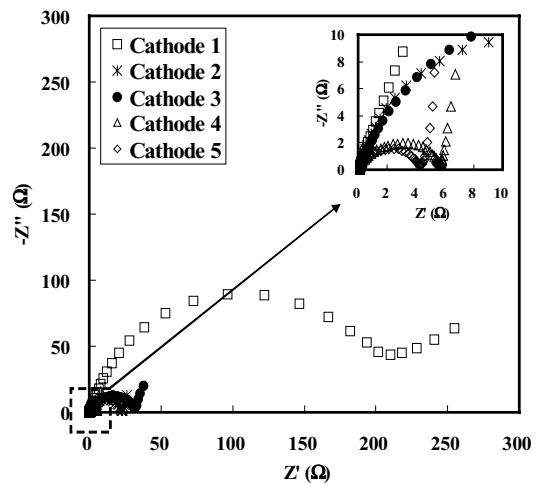


Fig. 4. Impedance spectra presented as Nyquist plots for cathodes with various binders.

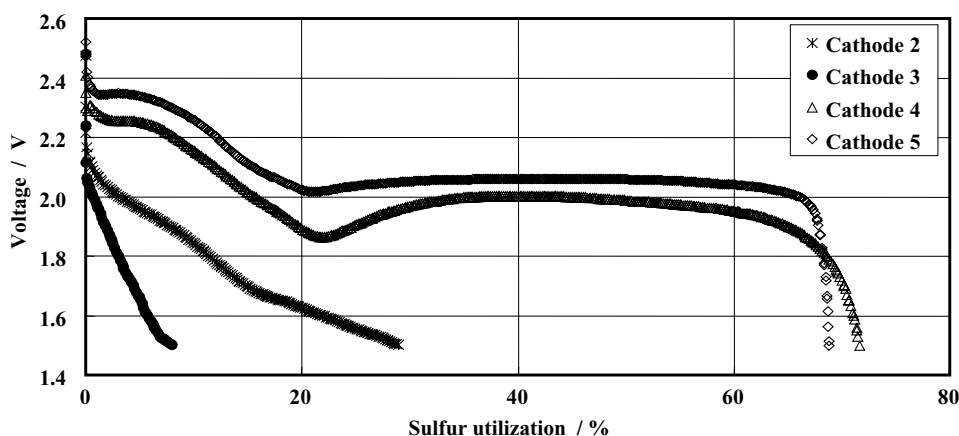


Fig. 5. Discharge profile of lithium-sulfur batteries with various cathodes.

The properties of the interface between the electrode and the electrolyte determines the performance of a rechargeable lithium-sulfur battery. The ac impedance spectrum was measured to investigate the interface between the cathode and the electrolyte. For an assembled cell, the impedance response was measured at open-circuit voltage before discharge. The results are presented in Fig. 4. Cells with cathodes that contain PTFE + PVA or PTFE + CMC display smaller interfacial resistances than those with PVP only as a binder. This means that a cathode with a large SSA reduces the interfacial resistance due to the increased contact area between the cathode composite materials and the electrolyte.

To examine the effects of the surface area of the cathode on discharge performance, cells with cathodes using various binders were discharged at 15 mA. The results are given in Fig. 5. The utilization of sulfur and the working voltage of the cells with PTFE are much higher than those of cells with PVP. For the cathode with PTFE binder, it is found that the operating voltage of the cell with CMC is higher than that of the cell with PVA, but that the sulfur utilization in both these cells is similar. This can be explained by the fact that the cell with a cathode based on PTFE has a larger surface area, as shown in Fig. 3, and a lower interfacial resistance, as shown in Fig. 4. The cell with the largest interfacial resistance (20 wt.% PVA, cathode 1) gave no discharge capacities. The results indicate that the power density and sulfur utilization of cells is related to the binder type mixed in the cathode. In particular, the introduction of PTFE will enhance the performance of lithium-sulfur batteries.

4. Conclusions

Cathodes prepared for lithium batteries have pores that are distributed mainly in the range of 20–0.05 μm diame-

ter. This feature is independent of the type of binder that is mixed in the cathode. Pore area is principally affected by pores with diameters of less than 0.05 μm . The presence of PTFE in the cathode develops pores with large surface area and reduces the resistance of the interface between the cathode and the electrolyte. The surface area increases with increasing PTFE content in the cathode. Also, cells with PTFE as binder exhibit higher operating voltage and capacity compared with those with PVP. The cathode composite material with PTFE + CMC (18:2 by weight) gives the greatest enhancement of capacity. The surface area of this cathode composite material is about $10\text{ m}^2\text{ g}^{-1}$.

Acknowledgements

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