The Effect of Binders on the Performance and Degradation of the Lithium/Sulfur Battery Assembled in the Discharged State

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Capacity fading on cycling of lithium/sulfur batteries may result from at least four processes: increase of SEI thickness resistance, loss of cathode capacity (precipitation of sulfur species outside the cathode), agglomeration and thickening of sulfur species and increase in cell impedance as a result of reduction of the electrolyte. A very important issue that has not been properly addressed up to now is the influence of the type and content of the cathode binder on the cell parameters and on the electrochemical performance of lithium/sulfur batteries. We present here a detailed analysis and discussion of the electrochemical behavior, during prolonged cycling, of Li2S-based cathodes containing five different binders. The binders under investigation are: poly(vinylidene fluoride) (PVDF-HFP), polyvinylpyrrolidone (PVP), mix of PVP with polyethylene imine (PEI), polyaniline (PANI) and lithium polycrylate (LiPAA). Sulfur utilization in the cathode follows the order of LiPAA > PVP > PEI > PVP > PVDF-HFP > PANI. Depending on the type of binder, cells provide 500 to 1400 mAh/g (S), 94.6–98.0% faradaic efficiency and enable more than 500 reversible cycles.

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several molar). On the other hand, during charge, the polysulphide concentration near the anode decreases. The reactions of polysulphides with lithium are complex; short ones are expected to cause precipitation of Li$_2$S and Li$_2$S$_2$ as lithium-corrosion products, while long polysulphides may partially dissolve Li$_2$S and Li$_2$S$_2$ particles from the SEI. This process leads to the accumulation on the anode of corrosion products (including Li$_2$S and Li$_2$S$_2$) and thus to the thickening of the primary and the secondary SEI. This shuttle mechanism of polysulphides results in reduction of the faradaic efficiency of the battery, in some cases to below 70%.~\cite{1,2,23} Many efforts have been made to minimize the reactions of polysulphides with the anode and to minimize their transport from the cathode to the anode. To summarize, the methods of overcoming the challenges of the Li/S battery include: reducing the solubility of the polysulphides by adding toluene to THF,~\cite{2} increasing the concentration of the supporting electrolyte,~\cite{1} encapsulation of the sulfur species (S or Li$_2$S) in several types of cages~\cite{24,26} and using polysulphide barriers and modified separators.~\cite{27,28} Modification of the electrolyte by the addition of nitrate, as proposed by Aurbach,~\cite{30} and film formation on the anode by its reaction with (CH$_3$)$_3$SiCl,~\cite{31} were found to minimize the reaction of polysulphides with the anode, thus leading to longer cycle life.

A very important issue, one that has not been properly addressed up to now, is the influence of the type and content of cathode binder on the electrochemical performance of lithium/sulfur batteries. Gau Liu et al.~\cite{32} studied the effects of some binders, including PFM (9,9-diocytfluorene-co-fluorene-co-methylbenzoic ester) PEDOT-PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) and PVP (poly(vinylpyrrolidone)), on sulfur-based cathodes. Lacey et al.~\cite{33} studied PVP, polyethylene oxide (PEO) and carboxymethyl cellulose-styrene-butadiene rubber (CMC-SBR) as binders for sulfur-based cathodes. With Li$_2$S as starting cathode material, except for the common PVDF binder, only PVP mixed with PEO has been studied.~\cite{34}

We report here a detailed analysis and discussion of the electrochemical behavior of Li$_2$S-based cathodes containing five different binders during prolonged cycling of a sulfur battery. The binders under investigation are: poly(vinylidene fluoride) (PVDF-HFP), polyvinylpyrrolidone (PVP), polyaniline (PANI), mix of PVP and PEI (polyethylene imine) and lithium polyacrylate (LiPAA).

**Experimental**

### Materials.

Commercial AR Li$_2$S powder (Aldrich), MWCNTs (SkySpring) and Timrex 300 (SpecialChem), were used as starting materials for active-powder preparation. PVDF-HFP 2801 (Kynar), PANI (emeraldine base, Mw = 50000, Aldrich), PVP (Mw = 56000, Fluka), binders, Li$_2$S, MWCNT, Timrex 300 and XC72 carbon were vacuum dried at 100 °C overnight prior to use. PEO (Mw = 500000, Aldrich) was dried at 60 °C, LiPAA was froze and dried under vacuum in Leofilizer (Heto DRYWINNER). While in the text we write PVDF abbreviation, actually PVDF-HFP binder was used in all the tests.

### Electrode preparation.

The active material for the cathode was produced by wet ball milling of 50% Li$_2$S, 40% Timrex 300 and 10% MWCNT in heptane for four hours at 450 rpm. This preparation procedure of the cathodes was the same for all binders used. The active powder was dispersed in a solution of the binder in N-methyl-2-pyrrolidone (NMP) (anhydrous 99.5%) except for LiPAA which was dispersed in THF. The cathode-powder dispersion was left overnight under magnetic stirring and cast on 15 μm carbon-coated Al foil. The cathodes were left overnight in an Ar-atmosphere glove box (MBraun) and then dried under vacuum at 120 °C for four hours. The weight ratio of active powder to binder was 90:10 for PVDF and PVP, 93:7 for PANI and LiPAA and 94:6 for PVDF: PEI (5:1) binders.

### Battery assembly and performance evaluation.

Coin cells (CR2032) were assembled in an Ar-atmosphere glove box (MBraun). The cathode was supported on a carbon-coated aluminum foil, two layers of Celgard 2400 separator (Celgard, USA) and Li foil (Rockwood Lithium). The electrolyte was 2 M bis(trifluoromethanesulfonyl)imide (LiTFSI) in dimethoxyethane (DME):1.3-dioxalane (DIOX) (1:1, v:v) with 0.15 M LiNO$_3$ as an additive. The cells were equilibrated for 12 hours before testing was begun. Typically, the mass loading of the electrode was ∼1 mg.cm$^{-2}$. Cells were charged and discharged over a voltage range of 1.8–3.6 V for the first cycle and between 2.8 V and 1.8 V for the remaining cycles. The cells were tested at C/10 for the first cycle, C/15 for the following ∼20 cycles, and C/10 thereafter as a durability test. The value of the 1 C rate for Li$_2$S is defined here as 1166 mA.g$^{-1}$. For these cycling tests, an Arbin SB2000 battery-testing station (Arbin Instruments, USA), BioLogic VMP3 system or MACCOR series 2000 system was used.

EIS of the batteries was carried out with the use of either BioLogic VMP3 system or Solartron over the range of 0.01 Hz to 1 MHz. The data were analyzed with the use of EC-Lab software. The following parameters were determined: SEI resistance (R$_{SEI}$), cathode charge-transfer-reaction resistance (R$_{c}$), Warburg parameter (W) and bulk resistance (R$_{b}$). Not in all cases we were able to determine all these parameters and we present here only those that are in good agreement with the equivalent circuit.

### Results and Discussion

#### Cycling performance of cathodes with different binders.

Beginning with Li$_2$S as the cathode-active material has two major benefits: it can be coupled to a safer anode such as silicon, tin or graphite (instead of metallic lithium), and building the cell in the most expanded state helps to overcome the sulfur cathode distortion when it expands from sulfur to Li$_2$S. PVDF is known as the common binder with no functional groups or any kind of ionic or electronic conductivity. PVP has amide carbonyl functional groups that can bind relatively strongly both to Li$_2$S and polysulphides, thus reducing the loss of active material as a dissolved polysulphide.~\cite{13,24,27,34} It is also believed to act as a redox mediator. PANI also has a nitrogen atom that may act as a polysulphide mediator. PANI PVDF-HFP LiPAA PVP PEI (a) Formulas of the binders: PANI, PVDF, LiPAA, PVP, and PEI. (b) Cycling of cathodes with different binders at C/10. Insert PANI-based and PVDF-based cathodes at prolonged cycling. Figure 1.

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**Figure 1.** (a) Formulas of the binders: PANI, PVDF, LiPAA, PVP, and PEI. (b) Cycling of cathodes with different binders at C/10. Insert PANI-based and PVDF-based cathodes at prolonged cycling.
Table 1. Effect of binders on: \(Q_{\text{loss}}\), \(Q_{\text{1disc}}\), Current Efficiency and Energy Efficiency.

| Binder   | \(Q_{\text{loss}}\) (%) | \(Q_{\text{1disc}}\) (mAh/gS) | Current Efficiency (%) | Energy Efficiency (%) |
|----------|------------------------|-------------------------------|------------------------|-----------------------|
| PANI     | 0.14                   | 623                           | 94.7                   | 87                    |
| PVP:PEI | 0.15                   | 960                           | 96.7                   | 89.5                  |
| PVDF     | 0.2                    | 778                           | 96.3                   | 89.4                  |
| PVP      | 0.25                   | 889                           | 98.0                   | 89.2                  |
| LiPAA    | 0.26                   | 1184                          | 97.3                   | 90.2                  |

utilization (the initial capacity - \(Q_{\text{in}}\)) and the rate of capacity fading. The highest initial capacity (1200 mAh/gS) was found for LiPAA and the lowest (600 mAh/gS) - for PANI. \(Q_{\text{in}}\) follows the order (Figure 1b and Table I) LiPAA > PVP:PEI > PVP > PVDF > PANI. We suggest that the more open and porous morphology of the cathodes, followed by better wettability (see Figure 7) and ion-conducting capability of LiPAA and PEI binders may explain the difference in \(Q_{\text{in}}\). Cells employing LiPAA and PANI cathode binders run for about 500 cycles, (see inset); (other cells were not considered because of the limitation of the number of available channels in our equipment). Figure 2 depicts charge- and discharge voltage profiles of all the cells with different binders. The profiles of the first cycle differ from those of the following cycles. The end voltage of the first charge is 3.6 V and for the rest, it is 2.8 V. Charging the cells to a voltage lower than 3.6 V for the first cycle, provides lower sulfur utilization. The charge/discharge mechanism of the lithium/sulfur battery is very complex. It depends on many parameters, including type of binder, type of electrolyte, type and content of carbon, temperature and current density. Many reports have been recently published, which lead to a better understanding of these processes.\(^{2,10,25}\) To simplify, the higher sloping plateau, from 2.5 to about 2.1 V, associated with the reduction of sulfur to Li_{2}S_{4}, we denote as \(Q_{\text{H}}\), the second plateau at about 2.1 V, and down to 1.8 V, is associated with the reduction of Li_{2}S_{4} to Li_{2}S, is denoted as \(Q_{\text{L}}\). However, the situation is much more complex and the reactions are not complete either on charge or on discharge. Polysulfides of different stoichiometry are involved in the charge/discharge process.\(^{2,10,25}\) We have found that the type of binder affects both \(Q_{\text{H}}\), \(Q_{\text{L}}\) (Table II) and their sum, denoted as \(Q_{\text{T}}\). For three binders, PVP:PEI, PVP and LiPAA, \(Q_{\text{H}}\) is about 30% of \(Q_{\text{T}}\). However, in the case of PVDF, it is about 40%, and for PANI, \(Q_{\text{H}}\) is half of \(Q_{\text{T}}\). In addition, PANI cells have the lowest current efficiency in the first cycle (Figure 2). This may result from precipitation of sulfur species outside the cathode, and so they are not available for the following discharge step. It is interesting to note that for all binders, the \(Q_{\text{H}}/Q_{\text{T}}\) ratio does not change from cycle 10 to cycle 200, despite the fact that the cell capacity drops by more than 30% (Table II). The constant \(Q_{\text{H}}/Q_{\text{T}}\) ratio indicates that the capacity-fading mechanism is the same for both \(Q_{\text{H}}\) and \(Q_{\text{T}}\). In the case of PANI, the second (lower) voltage plateau is similar to that of all other binders. However, the reduction from Li_{2}S_{4} to Li_{2}S is less effective (a small \(Q_{\text{L}}\) value). The current efficiency of all cells is quite high, between 94.6% (PANI) to 98% (PVDF) and the energy efficiency (Table I) varies between 87% (PANI) to 90.2% (LiPAA), close to that of lithium-ion batteries. It is well established that the

Table II. Effect of cycling and binders on \(Q_{\text{T}}, Q_{\text{L}}, \) and \(Q_{\text{H}}\).

| Binder   | \(Q_{\text{loss}}\) (%) | \(Q_{\text{T}}\) (mAh/gS) | \(Q_{\text{H}}/Q_{\text{L}}\) (%) | \(Q_{\text{L}}/Q_{\text{T}}\) (%) | \(Q_{\text{T}}\) (mAh/gS) | \(Q_{\text{H}}/Q_{\text{T}}\) (%) | \(Q_{\text{L}}/Q_{\text{T}}\) (%) |
|----------|------------------------|----------------------------|-------------------------------|-------------------------------|------------------------|-------------------------------|-------------------------------|
| PANI     | 0.14                   | 529                        | 50                            | 50                            | 361                    | 54                            | 46                            |
| PVP:PEI | 0.15                   | 796                        | 31                            | 69                            | 358                    | 32                            | 68                            |
| PVDF     | 0.2                    | 653                        | 39                            | 61                            | 455                    | 38                            | 62                            |
| PVP      | 0.25                   | 717                        | 32                            | 68                            | 473                    | 33                            | 67                            |
| LiPAA    | 0.26                   | 907                        | 31                            | 69                            | 554                    | 31                            | 69                            |

Figure 2. (a-c) Voltage profiles of the 1st, 10th and 200th cycles of Li/Li_{2}S cells with LiPAA, PVP:PEI, PVP, PANI and PVDF based cathodes.
soluble polysulfides act as a current “thief”. Long polysulfides move from the cathode to the anode, are reduced to shorter polysulfides by the anode and move back to the cathode where they are reoxidized to long polysulfides. In addition, during cycling, a thicker SEI may be formed by precipitation of Li$_2$S and LiNO$_3$ discharge products on the surface of the anode, leading to higher cell impedance and thus to capacity fading. The rate of capacity fading per cycle (Table I) is lowest for PANI (0.14%) and PVP:PEI (0.15%) and highest for LiPAA (0.26%). In general, capacity fading is inversely proportional to the initial capacity. For all binders, the capacity fading per cycle for the first 20 cycles (Figure 3a), is up to one order of magnitude greater than the multistep oxidation of sulfur may occur via the formation of Li$_2$S$_2$ according to the scheme Li$_2$S$_2$ $\rightarrow$ Li$_2$S. On prolonged cycling, the position and intensity of the dQ/dV curves of the PVP:PEI cathode almost coincides with the maximum of the first sharp charge peak at 2.8 V in the dQ/dV charge curve of the PVDF cathode. Here, even more clearly than in Figure 2b–2c, one can see that the PVP:PEI cathode (Figure 5b) shows lower charge/discharge overpotential (57 mV) of the first step of sulfur oxidation than do the PVDF and PANI cathodes. We can speculate, therefore, that in the PVP:PEI cathode, the multistep oxidation of sulfur may occur via the formation of Li$_2$S$_2$ according to the scheme Li$_2$S $\rightarrow$ Li$_2$S$_2$. On prolonged cycling, swelling of PVDF and PANI in DME-DOL electrolyte followed by increased tortuosity in the cathode may, in electrochemical conversion of Li$_2$S$_4$ to Li$_2$S. The two dQ/dV peaks seen in dQ/dV plots of PANI and PVDF cells (Figure 5a) at 2.27 V, associated with the S-to-Li$_2$S reaction, are broad and reflect slow kinetics. The narrow peaks at 2.08 and 2.09 V show fast kinetics of electrochemical conversion of Li$_2$S$_4$ to Li$_2$S. The two dQ/dV peaks on charge are much closer to each other, than are the corresponding peaks on discharge. This results in different charge/discharge overpotentials of the Li$_2$S ↔ Li$_2$S$_2$ and Li$_2$S$\rightarrow$ S reactions. Hence, despite the slower kinetics, the charge/discharge Li$_2$S$_2$ ↔ S overpotential is only 20 mV, while that of Li$_2$S$\rightarrow$ Li$_2$S$_2$ is about 100 mV. When comparing the dQ/dV curves of PVDF and PVP cathodes the similarity of discharge profiles stands out, while the charge profiles diverge. In the dQ/dV charge curves of the PVP:PEI cell, three peaks of different intensity and area can be distinguished. It is interesting that the maximum of the broad intermediate charge peak of the PVP:PEI cathode almost coincides with the maximum of the first sharp charge peak at 2.8 V in the dQ/dV charge curve of the PVDF cathode. Here, even more clearly than in Figure 2b–2c, one can see that the PVP:PEI cathode (Figure 5b) shows lower charge/discharge overpotential (57 mV) of the first step of sulfur oxidation than do the PVDF and PANI cathodes.

**dQ/dV curves.**—The voltage plateaus of the charge/discharge profiles appear as well pronounced peaks in normalized dQ/dV curves. The integrals of the peaks are associated with the relative capacities of the different steps in the charge/discharge reactions. The discharge peaks seen in dQ/dV plots of PANI and PVDF cells (Figure 5a) at 2.27 V, associated with the S-to-Li$_2$S$_2$ reaction, are broad and reflect slow kinetics. The narrow peaks at 2.08 and 2.09 V show fast kinetics of electrochemical conversion of Li$_2$S$_4$ to Li$_2$S. The two dQ/dV peaks on charge are much closer to each other, than are the corresponding peaks on discharge. This results in different charge/discharge overpotentials of the Li$_2$S ↔ Li$_2$S$_2$ and Li$_2$S$\rightarrow$ S reactions. Hence, despite the slower kinetics, the charge/discharge Li$_2$S$_2$ ↔ S overpotential is only 20 mV, while that of Li$_2$S$\rightarrow$ Li$_2$S$_2$ is about 100 mV. When comparing the dQ/dV curves of PVDF and PVP cathodes the similarity of discharge profiles stands out, while the charge profiles diverge. In the dQ/dV charge curves of the PVP:PEI cell, three peaks of different intensity and area can be distinguished. It is interesting that the maximum of the broad intermediate charge peak of the PVP:PEI cathode almost coincides with the maximum of the first sharp charge peak at 2.8 V in the dQ/dV charge curve of the PVDF cathode. Here, even more clearly than in Figure 2b–2c, one can see that the PVP:PEI cathode (Figure 5b) shows lower charge/discharge overpotential (57 mV) of the first step of sulfur oxidation than do the PVDF and PANI cathodes. We can speculate, therefore, that in the PVP:PEI cathode the multistep oxidation of sulfur may occur via the formation of Li$_2$S$_2$ according to the scheme Li$_2$S $\rightarrow$ Li$_2$S$_2$ $\rightarrow$ Li$_2$S$_3$ $\rightarrow$ S. On prolonged cycling, the position and intensity of the dQ/dV curves of the PVP:PEI cathode do not change (Figure 5c), indicating high electrochemical stability of the cell. Similar behavior was observed for the LiPAA cathode. While on cycling, the shape of the dQ/dV charge plots of the PVDF cathode (Figure 5d) becomes similar to that of the PVP:PEI cathode, the charge/discharge overpotential of the sulfur-oxidation reaction remains higher. Therefore, in spite of the same capacity fading for both discharge steps in PVP:PEI, PVDF and PANI cathodes, higher charge/discharge overpotential and/or different charge pathway deteriorates the performance of PVDF and PANI cells, particularly during initial cycling (up to 20–25 cycles). Swelling of PVDF and PANI in DME-DOL electrolyte followed by increased tortuosity in the cathode may, in
Figure 5. Effect of binders on dQ/dV profiles.

Figure 6. Nyquist plots of Li₂S/Li batteries comprising cathodes with different binders. Inset - equivalent circuit used for fitting.
After cycling in Figure 7. To study the effect of binders on the morphology of the cathodes, both in fully charged and discharged states, pores of the fresh cathodes as well as in cycled electrodes. In the SEM images of some cathodes before and after cycling are shown in Figure 7. To study the effect of binders on the morphology of the cathodes on prolonged cycling, the cells are disassembled both in fully charged and discharged states, and the cathodes are thoroughly washed and dried. The differences in morphology may be observed in the fresh cathodes as well as in cycled electrodes. In the SEM images of cycled cathodes, both in fully charged and discharged states, pores are blocked. The differences in morphology may indicate the different amounts of precipitated sulfur and sulfide species. After charge, the LiPAA cathode looks clear and porous compared to the other binders.

### Table III. EIS analysis parameters for cycled PVDF-based cathode.

| Cycles | R₀ (ohm) | R₁ (ohm) | R₂ (ohm) | W₂ (ohm s⁻¹) |
|--------|----------|----------|----------|--------------|
| 19     | 9.9      | 103.7    | 91.9     | 18.5         |
| 35     | 11.6     | 89.3     | 245.7    | 45.7         |
| 205    | 8.0      | 77.4     | 1228     | 1813         |

increased tortuosity caused by swelling of PVDF by the electrolyte. This, in turn, is followed by a decrease in the rate of diffusion of the lithium cation, in agreement with Deng et al. 38

SEM images of Li₂S cathodes with PVDF and LiPAA-based binders in the fully charged and discharged states, and the cathodes are thoroughly washed and dried. The differences in morphology may be observed in the fresh cathodes as well as in cycled electrodes. In the SEM images of cycled cathodes, both in fully charged and discharged states, pores are blocked. The differences in morphology may indicate the different amounts of precipitated sulfur and sulfide species. After charge, the LiPAA cathode looks clear and porous compared to the other binders.

### Summary

Five polymers with different surface-functional groups and their mix, namely PVDF-HFP, PVP, PANI, LiPAA and PVP-PEI, were tested as binders in Li₂S-based cathodes of lithium/sulfur batteries. It was found that the cathode binders affect both the utilization of sulfur and the rate of capacity fading. The initial highest capacity (1200 mAh/gS) was found for LiPAA and the lowest (600 mAh/gS) for PANI. For all binders, the capacity fading per cycle for the first 20 cycles is up to one order of magnitude greater than that for cycles 21 to 200; it is lowest (0.88%) for PVP:PEI and highest for PVDF-HFP (1.47%). The capacity fading per cycle for cycles 21 to 200 is between 0.8% (PANI) and 0.19% for LiPAA. Analysis of the dQ/dV curves provides evidence for different ion transport mechanisms in the cells with PVDF and PANI cathodes as compared to those with PVP:PVP and LiPAA cathodes. For the former the charge occurs as follows: Li₂S → Li₂S₄ → S. For the latter, an additional low-overpotential step Li₂S → Li₂S₄ facilitates high electrochemical stability of the cells.

The cells with LiPAA and mix of PVP:PVP delivered 550 mAh/gS reversible capacity after cycle 250 as compared to 438 mAh/gS of common PVDF-HFP binder. Depending on the type and content of binder, cells provide 500 to 1400 mAh/gS, 94.6–98% faradaic efficiency and enable more than 500 reversible cycles. We believe than the amino groups of PEI and the PAA oxygens interact with sulfide and polysulfide species to promote a higher stability of battery.

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### References

1. B. Scrosati, J. Hassoun, and Y.-K. Sun, *Energy Environ. Sci.*, 4, 3287 (2011).
2. X. Ji and L. F. Nazar, *J. Mater. Chem.*, 20, 9821 (2010).
3. A. Manthiram, Y. Fu, and Y.-S. Su, *Accounts of chemical research*, 46, 1125 (2013).
4. S. Urbonait, T. Poux, and P. Novák, *Adv. Energy Mater.*, 5, 1500118 (2015).
5. Z. W. Seh, H. Wang, P.-C. Hsu, Q. Zhang, W. Li, G. Zheng, H. Yao, and Y. Cui, *Adv. Energy Mater.*, 5, 1500117 (2015).
6. D. A. Nole and V. Moss, *U.S. Pat. 3,532,543, “Battery employing lithium - sulfur electrodes with non-aqueous electrolyte” 1970.
7. R. D. Rauh, M. A. Abraham, G. F. Pearson, J. K. Surprenant, and S. B. Brummer, *J. Electrochem. Soc.*, 126, 523 (1979).
8. H. Yamin and E. Peled, *J. Power Sources*, 9, 281 (1983).
9. E. Peled, A. Gorenstein, M. Segal, and Y. Sternberg, *J. Power Sources*, 26, 269 (1989).
10. X. Ji, T. Lee, and L. F. Nazar, *Nature Materials*, 8, 500 (2009).
11. Y. S. Jung, D. Y. Oh, Y. J. Nam, and K. H. Park, *J. Chem.**, 55, 472 (2015).
12. K. Cai, M.-K. Song, E. J. Cairns, and Y. Zhang, *Nano Lett.*, 12, 6474 (2012).
13. Z. W. Seh, H. Wang, P.-C. Hsu, Q. Zhang, W. Li, G. Zheng, H. Yao, and Y. Cui, *Energy Environ. Sci.*, 7, 672 (2014).
14. F. Wu, T. T. Lee, N. Nitta, H. Kim, O. Borodin, and G. Yushin, *Adv. Mater.*, 27, 101 (2015).
15. Y. Yang, G. Zheng, S. Misra, J. Nelson, M. F. Toney, and Y. Cui, *Adv. Energy Mater.*, 134, 15387 (2012).
16. Y. Hwa, J. Zhao, and E. J. Cairns, *Nano Lett.*, 15, 3479 (2015).
17. F. Wu, J. T. Lee, F. Fan, N. Nitta, H. Kim, T. Zhu, and G. Yushin, *Adv. Mater.*, 27, 5579 (2015).
18. F. Wu, J. T. Lee, O. Borodin, and G. Yushin, *ACS Nano*, 10, 1333 (2016).
19. E. Peled, *J. Electrochem. Soc.*, 126, 2047 (1979).
20. E. Peled and D. Golodnitsky, SEI on lithium, graphite, disordered carbons and tin-based alloys, in SOLID-ELECTROLYTE INTERFACE (Eds., P. Balbuena and Y. Wang) Imperial College Press and World Scientific Publishers, 2004, 1
21. M. Barghamadi, A. S. Best, A. J. Blatt, A. P. Hollenkamp, P. J. Mahon, M. Musameh, and T. Ruther, *J. Power Sources*, 295, 212 (2015).
22. F. Wu, J. T. Lee, A. Magasinski, H. Kim, and G. Yushin, *Part. Part. Syst. Charact.*, 31, 639 (2014).
23. E. Peled, M. Alon, and D. Golodnitsky, Electrode compositions and alkal metal batteries comprising same, PCT/IL2015/050119.
24. Z. W. Seh, W. Li, J. J. Cha, G. Zheng, Y. Yang, M. T. McDowell, P.-C. Hsu, and Y. Cui, *Nat. Commun.*, 4, 1331 (2013).
25. X. Liang and L. F. Nazar, *ACS Nano*, 10, 4192 (2016).
26. Y.-S Su and A. Manthiram, *Chem. Commun.*, 48, 8817 (2012).

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**Figure 7.** SEM images of Li₂S cathodes with PVDF and LiPAA-based cathode.
27. H. Yao, K. Yan, W. Li, G. Zheng, D. Kong, Z. W. Seh, V. K. Narasimhan, Z. Lianga, and Y. Cui, *Energy Environ. Sci.*, 7, 3381 (2014).
28. J.-Y. Hwang, H. M. Kim, S.-K. Lee, J.-H. Lee, A. Abouimrane, M. A. Khaleel, I. Belharouak, A. Manthiram, and Y.K. Sun, *Adv. Energy Mater.*, 6, 1501480 (2016).
29. S.-H. Chung and A. Manthiram, *Adv. Funct. Mater.*, 24, 6105 (2014).
30. D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. S. Kelley, and J. Affinito, *J. Electrochem. Soc.*, 156, A694 (2009).
31. M. Wu, Z. Wen, J. Jin, and B. V. R. Chowdari, *ACS Appl. Mater. Interfaces*, 8, 16386 (2016).
32. G. Ai, Y. Dai, Y. Ye, W. Mao, Z. Wang, H. Zhao, Y. Chen, J. Zhu, Y. Fu, V. Battaglia, J. Guo, V. Srinivasan, and G. Liu, *Nano Energy*, 16, 28 (2015).
33. M. J. Lacey, F. Jeschulli, K. Edstrom, and D. Brandell, *J. Power Sources*, 264, 8 (2014).
34. Z. W. Seh, Q. Zhang, W. Li, G. Zheng, H. Yao, and Y. Cui, *Chem. Sci.*, 4, 3673 (2013).
35. M. Gvozdenovic, B. Jugovic, D. Jambrec, J. Stevanovic, and B. Grgur, *Zaatita materijala*, 53, 353 (2012).
36. N. P. W. Pieczonka, V. Borgel, B. Ziv, N. Leifer, V. Dargel, D. Aurbach, J.-H. Kim, Z. Liu, X. Huang, S. A. Krakhkovskiy, G. R. Goward, I. Halalay, B. R. Powell, and A. Manthiram, *Adv. Energy Mater.*, 5, 1501008 (2015).
37. S.S. Zhang, K. Xu, and T.R. Jow, *Electrochimica Acta*, 51, 1636 (2006).
38. E. Peled, *J. Electrochem. Soc.*, 126, 2047 (1979).
39. N. A. Canas, K. Hirose, B. Pascucci, N. Wagner, K. A. Friedrich, and R. Hiesgen, *Electrochimica Acta*, 97, 42 (2013).
40. Z. Deng, Z. Zhang, Y. Lai, J. Liu, J. Li, and Y. Liu, *J. Electrochem. Soc.*, 160, A553 (2013).