

Poly(amic acid) Lithium Salt as a Multi-Functional Binder for High Performance Lithium/Sulfur Battery Cathodes

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Water-soluble poly(amic acid) lithium (PAALi) salts were firstly used as the binders for lithium/sulfur battery. Benefiting plenty functional groups (amide and carboxylate), S@PAALi cathodes with sulfur loading of ca. 8.0 mg cm⁻² showed excellent performance compared to the conventional polymer binders (such as PVDF): initial capacities > 1200 mAh g⁻¹ and with > 84% retention after 130 cycles. This research provides a new approach to improving lithium-sulfur batteries by designing multi-functional binders.

Keywords: Lithium/sulfur battery; Water-soluble binder; Poly(amic acid) lithium; Electrochemistry

1. INTRODUCTION

Recently, lithium-sulfur batteries (Li-S batteries) have attracted a great amount of attention due to their high theoretical specific capacity (1675 mAh g⁻¹) and energy density (2600 Wh kg⁻¹). [1, 2] Furthermore, elemental sulfur benefits from advantages of its natural abundance, low cost and environmentally friendly. [3, 4] However, they are still faced with several challenges, such as low conductivity of sulfur phase, lithium polysulfide shuttling between the electrodes, large volumetric change during electrochemical cycling, which have hindered their practical applications. [5] To address these problems, tremendous efforts have been made to immobilize sulfur inside conducting host materials *e.g.* N-doped carbons, [6, 7] porous carbons, [8-11] hollow carbons [12, 13] and so on. These methods enormously enhance the performance of Li-S batteries. However, these methods are all commonly complex and they are not suitable for practical application.

In the fact, the binder as an important ingredient in battery functions can also improve the performance of Li-S batteries significantly by designing suitable functional group in it, [14, 15] such as,

carboxylate group,[16-20] carbonyl group,[21, 22] amino group,[23-26] amide group,[27-29] sulfonate group,[30-33] phosphate group,[34] hydroxyl group[35, 36] and ammonium group.[37-40] The main effects of these functional groups were divided into two aspects: absorbing polysulfides and increasing the ion-conducting ability. It has been proved that amide groups could create strong interactions between discharge products polysulfides to buffer the shuttle effect of sulfur cathodes,[27-29] and carboxylate groups (such as -COOLi) could provide good lithium-ion conduction and compensate for Li⁺ loss during cycling of cells.[16-18] However, there were few works reported about the combination of amide group and carboxylate group in one binder used in Li-S batteries.

Hence, in this paper, we introduced a kind of multi-functional poly(amic acid) lithium (PAALi) salt binder with plenty amide groups and carboxylate groups as efficient binder for Li-S batteries. Moreover, unlike conventional polymeric binders (PVDF), water based PAALi binders do not dissolve in electrolyte owing to the hydrophilic nature, and the solvent water is totally benign.

2. EXPERIMENTAL

2.1. Synthesis of the poly(amic acid) lithium (PAALi) salt binders

All reagents were commercially available and used as received without further purification. Pyromellitic dianhydride (PMDA) (> 98%), 4,4'-oxydianiline (ODA) (> 99%), p-phenylenediamine (PDA) (> 99%), N,N'-dimethylethylenediamine (DMEDA) (> 97%), N-methyl-2-pyrrolidone (NMP) (> 99%), acetone (>99%), lithium hydroxide (>99%) were purchased from Beijing Innochem Science & Technology Co., Ltd..

The poly(amic acid) lithium (PAALi) salt binders were synthesized according to the previous reports after a minor modification.[41, 42] Typically, 50 mmol ODA (or PDA or DMEDA) was fully dissolved in 150 mL NMP. The solution was continuously stirred at 0 ~ 15 °C with mechanical stirring and 46 mmol PMDA powder was added slowly within 40 min. The reaction mixture was stirred at room temperature for an additional 2 h, and 0.11 mol LiOH in 50 mL of H₂O was added slowly to the reaction mixture within 30 min, which was stirred for an additional 5 h at room temperature. The solid polymer binders were obtained by precipitation into 500 mL acetone. The crude products were washed with acetone and dried at 50 °C under vacuum for 2 days to give white solid for ODA (yellow solid for PDA or pale yellow solid for DMEDA).

2.2. Characterizations of PAALi binders

FTIR spectra were recorded on a FTIR spectrophotometer (Nicolet iS10) in the range of 4000 - 400 cm⁻¹ using KBr pellets to study the structures of PAALi binders.

2.3. Preparation of electrode and electrochemical measurements

A mixture of sulfur, KB and VGCF with a mass ratio of 77:13:10 was heated in a Teflon container at 155 °C for 12 hours to obtain the active materials. A mixture of 90 wt% active material and 10 wt%

PAALi binder was stirred in deionized water to form a homogeneous slurry via magnetic stirring. The electrode film was prepared by coating the slurry on an Al foil. The film was dried at 55 °C for 12 h in vacuum. The cathode with 10 wt% PVDF binder were prepared through the identical way described previous, except that deionized water was displaced by NMP. The sulfur loading densities for all the cathodes were between 7.5 and 8.4 mg cm⁻². The electrochemical measurements were carried out by using CR2032 coin cells, which were assembled in an Ar-filled glove box. A metallic lithium disk and a microporous polypropylene/polyethylene/polypropylene film were used as the anode and separator, respectively. The solution of 1 M Li(CF₃SO₂)₂N in DME : DOL (1:1, v/v) was utilized as the electrolyte. The electrochemical performance of coin cells at various C rates (1C = 1673 mA g⁻¹) in a voltage range of 1.8 - 2.8 V was determined using LANHECT2001A battery tester. Cyclic voltammetry (CV) characteristics of the electrodes were determined using Solartron 1287 / 1260 electrochemical system in the voltage range of 1.8 - 2.8 V or 0.1 - 3.0 V vs. Li/Li⁺ at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) experiments of the electrodes were conducted on a Solartron 1287 / 1260 electrochemical system in the frequency range from 0.1 to 10 kHz.

3. RESULTS AND DISCUSSION

Generally, PAALi can be synthesized by the copolymerization of dianhydride and diamine. To study the structure effect of PAALi binders, three different monomer of diamine (PDA, ODA and DMEDA) were chose and the corresponding binders were denoted as PAALi-PDA, PAALi-ODA and PAALi-DMEDA, respectively. The formulas of these binders were shown in Figure 1a. PAALi binders have plentiful carboxylate groups and amide groups, and the ratio of the two groups is 1:1. FTIR spectrum of PAALi binders were shown in Fig. 1b. The C=O stretching modes in amide groups for PAALi-PDA, PAALi-ODA and PAALi-DMEDA were at 1658 cm⁻¹, 1658 cm⁻¹ and 1666 cm⁻¹, respectively. The C=O asymmetric stretching modes and symmetric stretching modes in carboxylate groups for PAALi- PDA, PAALi-ODA and PAALi-DMEDA were at 1581 cm⁻¹ and 1407 cm⁻¹, 1605 cm⁻¹ and 1408 cm⁻¹, 1603 cm⁻¹ and 1404 cm⁻¹, respectively.

Electrochemical measurements were carried out to evaluate the applications of PAALi as the binders in Li-S batteries.

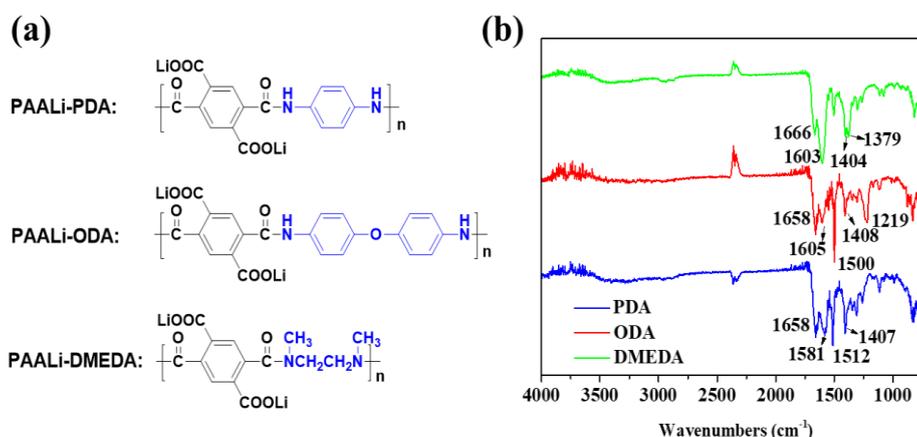


Figure 1. (a) Chemical structures and (b) FTIR spectra of the PAALi-PDA, PAALi-ODA and PAALi-DMEDA

The electrochemical stabilities of PAALi were first studied using cyclic voltammetry (CV), as shown in Fig. 2a, which demonstrated that the PAALi binders were all electrochemically stable between 1.5 and 3.0 V. The CV spectrums for the S@PAALi electrodes with sulfur loading of ca. 8.0 mg cm⁻² at a scan rate of 0.1 mV S⁻¹ were shown in Fig. 2b. Consistent with the CV curves of the common Li-S batteries, two generic reduction peaks were clearly observed for all of the PAALi binders, which correspond to the reduction of elemental sulfur to soluble polysulfides (Li₂S_x, 4 ≤ x ≤ 8) and then to the insoluble Li₂S₂/Li₂S, respectively. Compared with PAALi-ODA and PAALi-DMEDA, the second reduction peak of PAALi-PDA showed a higher peak current densities and considerably smaller overpotentials, which was due to increased sulfur utilization and faster reaction kinetics.[38]

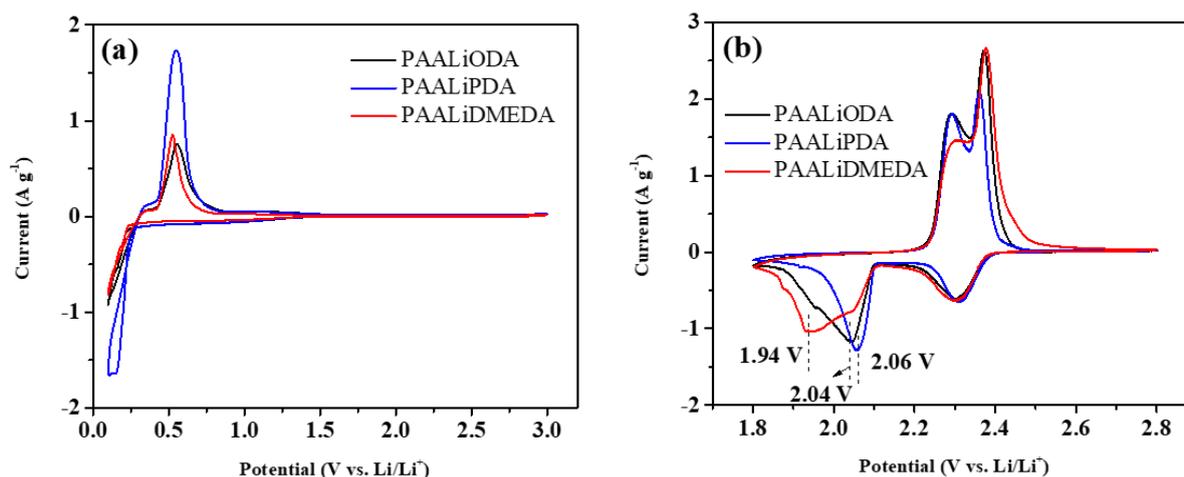


Figure 2. The cyclic voltammograms of pure PAALi (a) and S@PAALi cathode (b) in the potential range of 1.8 - 2.8 V vs. Li/Li⁺ at 0.1 mV s⁻¹.

The cycling performances and discharge/charge voltage profiles of S@PAALi and S@PVDF were shown in Fig. 3. From Fig. 3a-d, we can see that, compared with commonly used PVDF binder, high initial capacities were obtained: 1203.3 mAh g⁻¹ for PAALi-PDA, 1250.5 mAh g⁻¹ for PAALi-ODA, 1188.8 mAh g⁻¹ for PAALi-DMEDA at 0.1C, which indicates good ion-conducting capabilities of PAALi due to their plentiful carboxylate groups.[18] Moreover, the cycling performances of S@PAALi-PDA and S@PAALi-ODA were significantly better than those with S@PVDF. As shown in Fig. 3a and b, after 130 cycles, the capacities of S@PAALi-PDA and S@PAALi-ODA were stabilized at 1011.3 mA h⁻¹ with 84.1% retention and 1062.0 mA h⁻¹ with 84.9% retention, respectively. In contrast, the S@PVDF started at 928.8 mA h⁻¹ in the first cycle, but the specific capacity dropped severely to 552.2 mA h⁻¹ after the same number of cycles, which corresponds to only 59.5% capacity retention (Fig. 3d). The stable cycling performance imply that the PAALi-PDA and PAALi-ODA binders are benefit to confine polysulfides in the electrode, which dues to the lots of amide functional groups of PAALi binders.

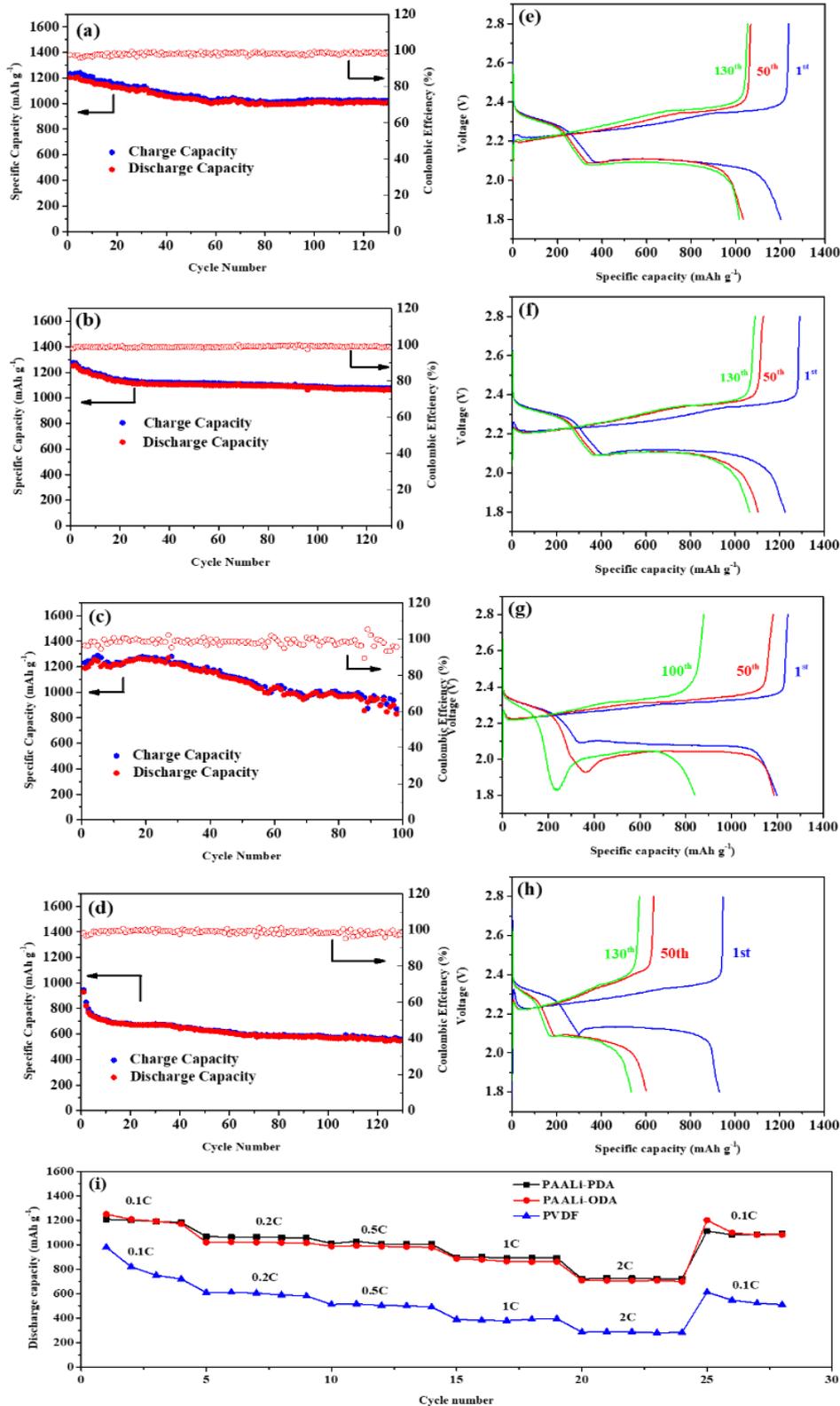


Figure 3. Cycling performance and Coulombic efficiency of (a) S@PAALi-PDA, (b) S@PAALi-ODA, (c) S@PAALi-DMEDA, (d) S@PVDF electrodes between 1.8 and 2.8 V at 0.1C with a sulfur loading density of ca. 8.0 mg cm⁻²; Discharge/charge voltage profiles with different cycles at 0.1C of (e) S@PAALi-PDA, (f) S@PAALi-ODA, (g) S@PAALi-DMEDA, (h) S@PAALi-PVDF electrodes; (i) Cycling performance for S@PAALi-PDA, S@PAALi-ODA and S@PAALi-PVDF at different rate.

As previous papers reported, the amide functional groups with high binding strength can construct effectual trap to confine the polysulfides within the cathode and inhibit the shuttling effect.[27, 29] Furthermore, the discharge/charge curves of S@PAALi-PDA and S@PAALi-ODA showed the typical two-plateau discharge/charge profile of Li-S cells (Fig. 3e and f), which could be assigned to the formation of long-chain polysulfides (high plateau at around 2.3 V) and short-chain polysulfides (low flat plateau at around 2.05 V).[8] Besides that, S@PAALi-PDA and S@PAALi-ODA also showed more excellent C-rate discharge performances from 0.1C to 2C compared with S@PVDF. Even at 2C rate, the specific capacity of S@PAALi-PDA and S@PAALi-ODA remained above 700 mAh g⁻¹, whereas the residual capacity of S@PVDF was only ca. 280 mAh g⁻¹.

It should be noted that, although S@PAALi-DMEDA exhibited a high capacity in the first cycle, a severely dropping trend of the capacity was maintained after 20th cycle, as shown in Fig. 3e. The discharge/charge voltage profiles of S@PAALi-DMEDA also showed an odd profile. For the first cycle, the discharge/charge plateau was agreed well with the common Li-S batteries, while, the second discharge plateau decreased with cycling (see Fig. 3g). It is consisted with the CV result, which showed a serious overpotential for the second reduction potential of PAALi-DMEDA. This may result from the poor adhesive property of PAALi-DMEDA and the weak bonding strength of amide functional groups in PAALi-DMEDA (the huge steric inhibition of N-CH₃ compared to N-H can decrease the affinity of amide with soluble polysulfides).

In order to gain the insight into the effect of PAALi binders on sulfur cathodes, Fig. 4 shows typical Nyquist plots of the sulfur cathodes with different binders before cycling and after 60 cycles. From Fig.4a, it can be seen that, before cycling, the internal resistance of the binders follow the order: PAALi-PDA < PAALi-ODA < PAALi-DMEDA < PVDF, which further verify the good ion-conducting capabilities of PAALi binders. After 60 cycles, both the internal resistance and charge transfer resistance of PAALi electrodes still lower than those of one with PVDF (Fig. 4b). This was due to the swelling effect of PVDF, which can impair the electrical contact between the cathode materials and current collector, causing the increase of the contact resistance and decreasing the charge-transfer ability.[43] Meanwhile, PVDF is an electronic and ionic insulator, which increases the interfacial resistance.[44] In contrast, the water-soluble PAALi binder shows a non-swelling property in organic electrolyte. Moreover, plentiful carboxylate groups and amide groups further increase the ion-conducting ability and absorb the polysulfides to decrease the agglomeration of Li₂S₂/Li₂S on the cathodes. For the three different structure PAALi binders, PAALi-PDA and PAALi-ODA showed more excellent conductivity both in electronics and ions transfer than those of PAALi-DMEDA. This may due to the lower adhesive property of PAALi-DMEDA than that of PAALi-PDA and PAALi-ODA. In addition, compared with PAALi-ODA, PAALi-PDA has a better electrochemical performance, which may benefit the greater density of the functional groups.

The electrochemical performances of Li-S batteries for PAALi binders and the other multifunctional binders with carboxylate groups and/or amide groups were also compared in Table 1. It can be obviously seen that PAALi binders showed the best performance even at a high sulfur loading density.

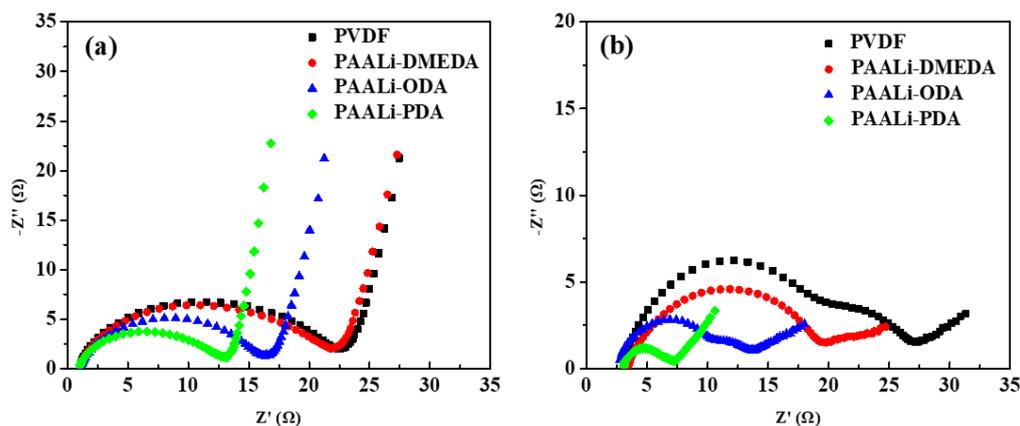


Figure 4. Nyquist plots of a Li-S batteries comprising cathodes with different binders in the frequency range of 100 kHz to 10 mHz: (a) before cycle, (b) after 60 cycles. Inset : the equivalent circuits.

Table 1. Typical multifunctional binders and the resulted electrochemical performance of Li-S batteries

Binders	Electrochemical performance	Sulfur loading density	Ref.
SBR-CMC	870 mA h g ⁻¹ at 0.06 C, capacity retention of 66.7% after 60 cycles	-	[16]
SBR-CMC	1046 mA h g ⁻¹ at 0.2 C, capacity retention of 78.5% after 50 cycles	0.45 - 0.64 mg cm ⁻²	[17]
LA132	1169 mA h g ⁻¹ at 0.2 C, capacity retention of 75.7% after 50 cycles	0.45 - 0.64 mg cm ⁻²	[17]
SA	990.8 mA h g ⁻¹ at 0.2 C, capacity retention of 67% after 50 cycles	0.45 - 0.64 mg cm ⁻²	[17]
LiPAA	1184 mA h g ⁻¹ at 0.1 C, capacity retention of 48% after 200 cycles	~ 0.5 mg cm ⁻²	[18]
Li ₄ PBI	790 mA h g ⁻¹ at 0.5 C, capacity retention of 60% after 400 cycles	~ 3.0 mg cm ⁻²	[19]
Maleate-PEG	1038 mA h g ⁻¹ at 0.1 C, capacity retention of 78% after 50 cycles	~ 6.0 mg cm ⁻²	[20]
PVP	1090 mA h g ⁻¹ at 0.2 C, capacity retention of 87.6% after 200 cycles	~ 1.4 mg cm ⁻²	[27]
G4COONa	971 mA h g ⁻¹ at 0.05 C, capacity retention of 73% after 100 cycles (0.2C)	~ 4.3 mg cm ⁻²	[28]
PAALi-PDA	1203.3 mA h g ⁻¹ at 0.1 C, capacity retention of 84.1% after 130 cycles	~ 8.0 mg cm ⁻²	This work
PAALi-ODA	1250 mA h g ⁻¹ at 0.1 C, capacity retention of 84.9% after 130 cycles	~ 8.0 mg cm ⁻²	This work
PAALi-DMEDA	1188.8 mA h g ⁻¹ at 0.1 C, capacity retention of 68.1% after 100 cycles	~ 8.0 mg cm ⁻²	This work

4. CONCLUSIONS

In summary, poly(amic acid) lithium (PAALi) salts for the first time have been successfully applied as binders for Li-S batteries. Due to their plenty functional groups (amide and carboxylate), S@PAALi-PDA and S@PAALi-ODA cathodes showed excellent cycling performance and specific capacity compared to the conventional polymer binders (such as PVDF). Moreover, the PAALi binders are readily soluble in water, which have the advantages of low cost and environmental benignity.

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