Chloric polycation binder enables rapid ionic transport in thick electrodes of high-energy aluminum-ion batteries

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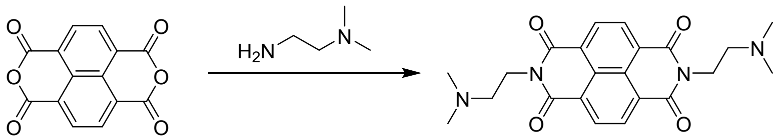
Synthetic procedures

N,N'-bis[(2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalene diimide



To a suspension of 1,4,6,8-tetracarboxilic dianhydride (2.3 g) in THF (20 ml) and H_2O (20 ml) is added 3 ml of 2-N,N-dimethylethylamine. The mixture is stirred for 8 hours at 80 °C. The mixture is then cooled down to r.t. The precipitate is collected on a filter and washed with water and ethanol to give a golden needle-like solid that is pure enough to carry out the next step (1.13 g, 32%). NMR results are consistent with the literature.

Polymerization of PHDMAC

1,6-dichlorohexane (400 mg), N^1,N^1,N^6,N^6-tetramethylhexane-1,6-diamine (440 mg) and 8 mL of H_2O are added to a round-bottom flask. The emulsion is stirred for four days at 100 °C, leading to a colorless solution which is carried out on the next step without working up.

Polymerization of PHDMAC-NDI

1,6-dibromohexane (314 mg), N^1,N^1,N^6,N^6-tetramethylhexane-1,6-diamine (200 mg) and N,N'-bis[(2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalene diimide (52.7 mg) are dissolved in 5ml of DMF. The solution is stirred for 2 hours at 130 °C, and a yellowish precipitate is obtained. 10 ml of deionized water is added to the mixture, and the precipitate dissolves. The yellow solution is further stirred for four days at 130 °C, concentrated under reduced pressure, and the remaining solid is redissolved in 100 ml of deionized water.

The anion exchange is carried out using a Dowex 1X8 chloride-formed anion exchange resin. A column of this resin is initially flushed with saturated brine and copious deionized water before loading with the aqueous polymer solution. The number of ionic equivalents in the column is above 100 fold higher than the number of PHDMAC-NDI equivalents passed through it. The solution is slowly passed through the ion exchange column, and the resulting PHDMAC-NDI is collected. The resulting aqueous solution is then concentrated before carrying out on next step.

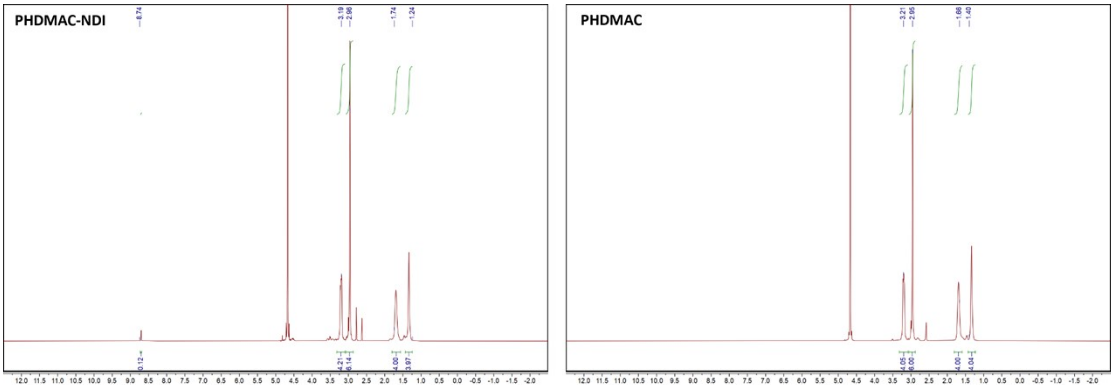


Fig. S1. ^{1}H NMR of PHDMAC and PHDMAC-NDI

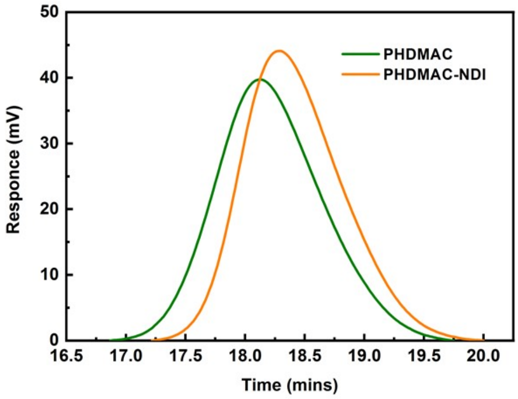


Fig. S2. Gel permeation chromatography (GPC) results of PHDMAC and PHDMAC-NDI

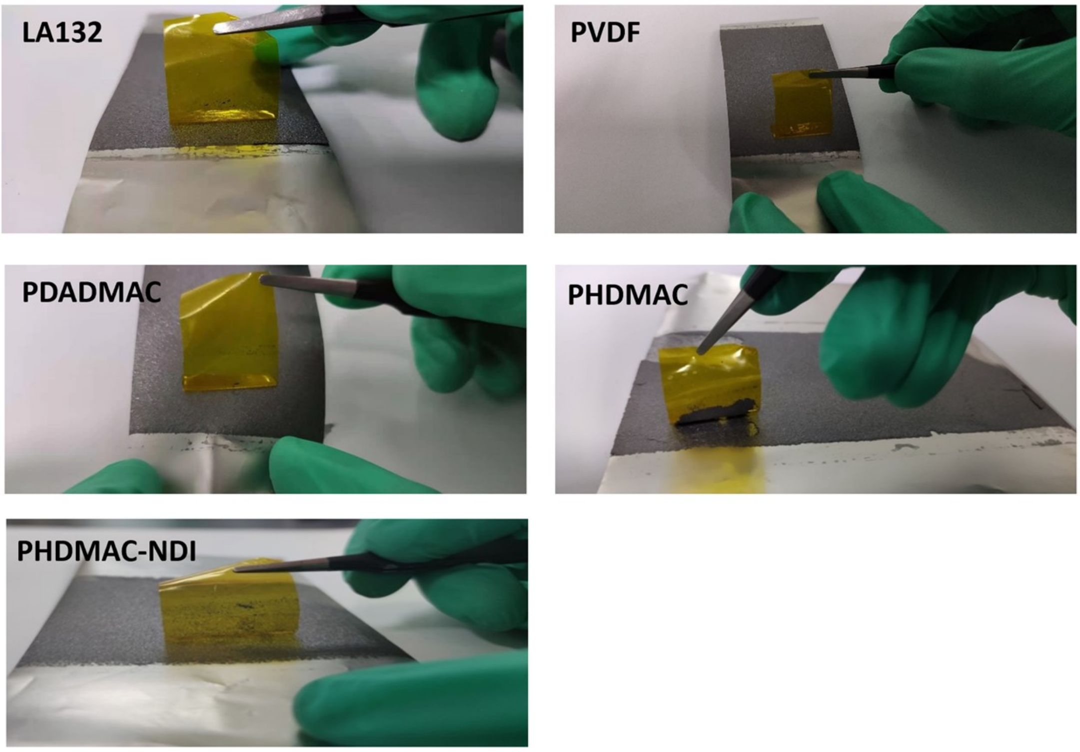


Fig. S3. Qualitative peeling-off testing of the pristine cathode based on LA132, PVDF, PDADMAC, PHDMAC, and PHDMAC-NDI

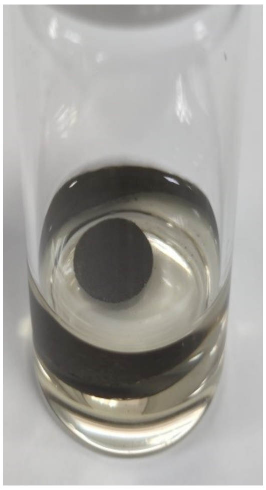


Fig. S4. Stability test results of the electrodes based on PDADMAC

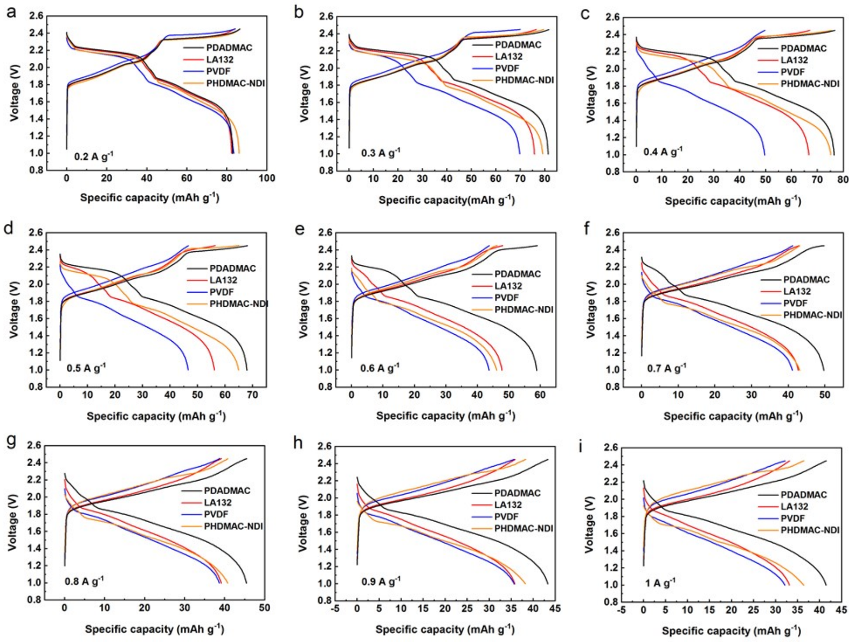


Fig. S5. Charge/Discharge curves of PDADMAC, LA132, PVDF, and PHDMAC-NDI-based AIBs at current density range from 0.2 to 1 A g^{-1} (with the loading of about 10 mg cm^{-2})

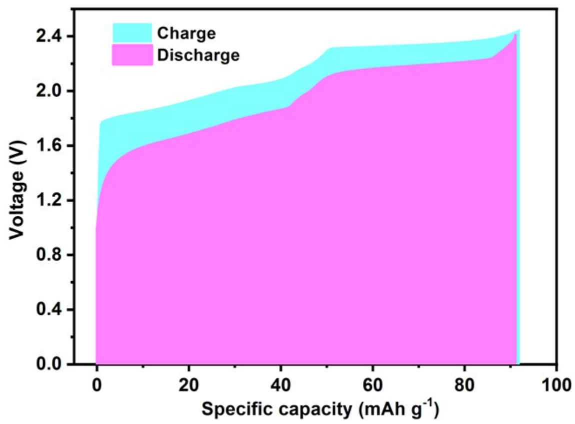


Fig. S6. In typical Charge/Discharge profiles of PDADMAC-based AIBs, the calculated energy efficiency is 89.5%. (450th cycle of the long-term performance at 0.19 A g^{-1}, with the loading of 10.6 mg cm^{-2})

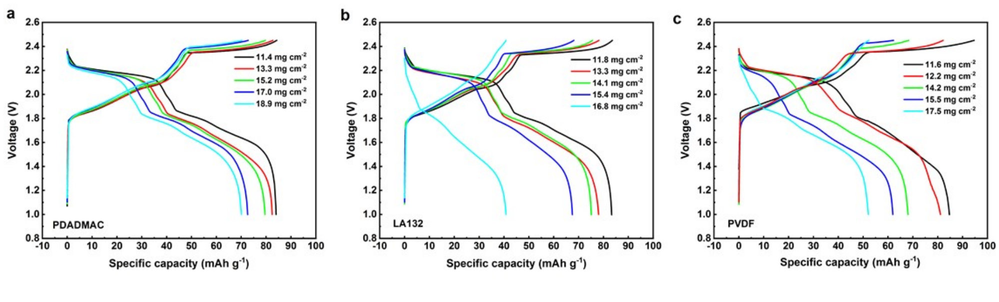


Fig. S7. Charge/Discharge curves of PDADMAC, LA132, and PVDF-based AIBs at different area loading (at 0.2 A g^{-1})

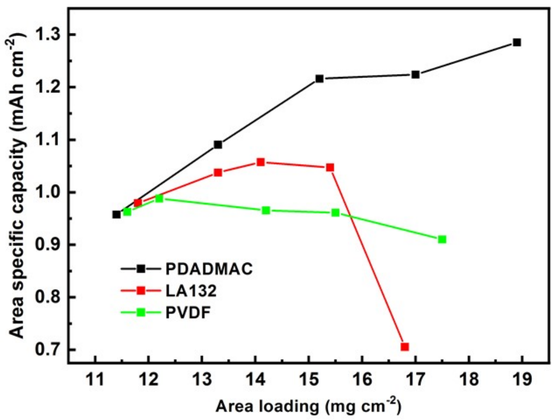


Fig. S8. The area-specific capacity of AIBs based on PDADMAC, LA132, and PVDF with area loading ranges from 11 to 19 mg cm^{-2} (at 0.2 A g^{-1})

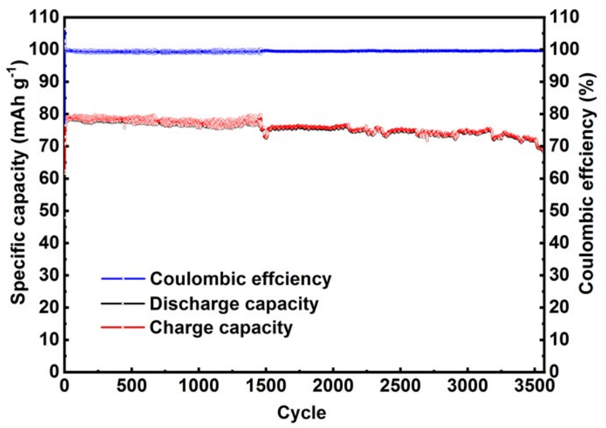


Fig. S9. Long-term cycling performance of PDADMAC-based AIBs at 0.2 A g^{-1}, with the loading of 14.2 mg cm^{-2}

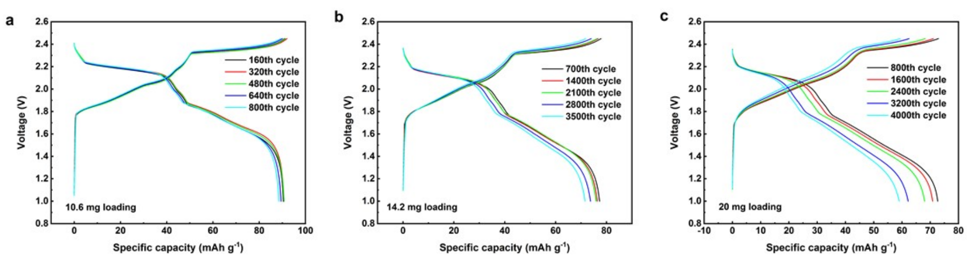


Fig. S10. Charge/Discharge curves of PDADMAC-based AIBs during cycling life at 0.2 A g^{-1}, with different area loading

Energy density calculation

The energy density is calculated with a specific capacity of 75 mAh g^{-1} for 20 mg cm^{-2} loading AIBs and 97 mAh g^{-1} for 5.46 mg cm^{-2} loading AIBs (both at 0.2 A g^{-1}), respectively. The Al and Mo foil collectors' thicknesses are 50 μm and 20 μm, respectively; The mess of the glass fiber separator is 3 mg cm^{-2} (200 μm thickness); The mass ratio of graphite and ILs electrolyte is 1/2.73 (w/w)。

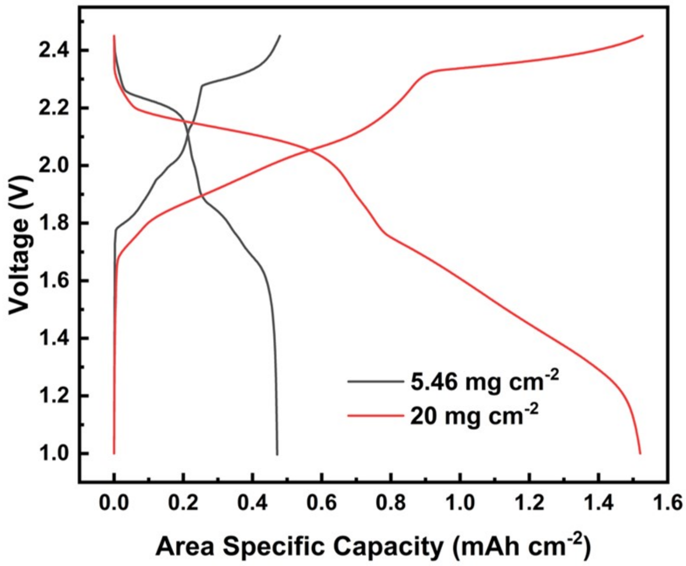


Fig. S11. The area specific capacity of AIBs of 5.46 mg cm^{-2} and 20 mg cm^{-2}

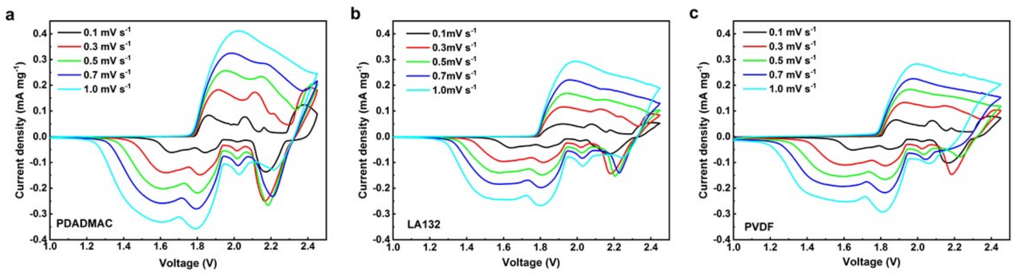


Fig. S12. CV curves of PDADMAC, LA132, and PVDF-based electrodes with different sweep rates (with a loading of about 15 mg cm^{-2})

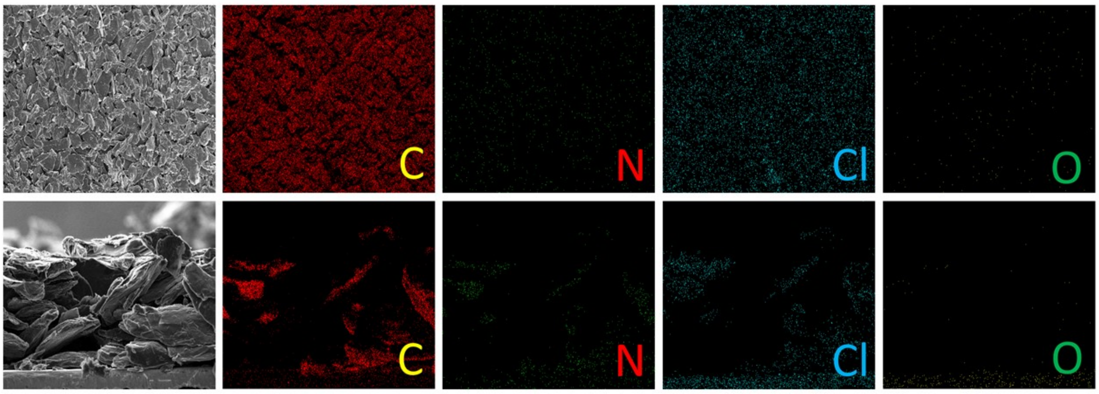


Fig. S13. SEM and EDS mapping images for C, N, Cl, and O of the pristine cathode based on PHDMAC-NDI (top row: surface view, bottom row: section view)

Fig. S14. The quartz cell for in-situ Raman spectroscopy study

Table S1. Calculated and XRD peak positions for stage 4-6 of $AlCl_4^-$ graphite intercalation compounds and the experimental data of PDADMAC, PVDF, and LA132 electrode and their corresponding capacity

	Calculated result	Experimental result of PDADMAC	Experimental result of PVDF	Experimental result of LA132
2θ of d(004+1)	22.7°	22.6°	-	-
2θ of d(005+1)	23.3°	23.4°	23.4°	23.4°
2θ of d(006+1)	23.7°	-	24.3°	24.3°
Capacity (mAh g^{-1})	-	72	36	42

Table S2. Molecular weights of binders and electron transfer resistance, Warburg impedance coefficient, and diffusion coefficient of electrode based on different binders

	LA132	PVDF	PDADMAC
Mw (kDa)	200~300	1000	400~500
Rct (Ω)	1.01	1.32	0.83
σ (Ω $s^{-1/2}$)	6.35	6.98	2.52
D (cm^2 s^{-1})	1.44 X 10^{-11}	1.22 X 10^{-11}	9.15 X 10^{-11}