Reinforced polyaniline-dodecyl benzene sulfonate hydrogel with well-aligned fibrous morphology as durable electrode materials for Zn-ion battery

Kairon Márcio de Oliveira

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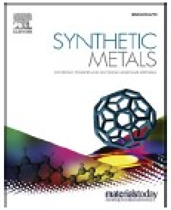
Synthetic Metals 274 (2021) 116721

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Reinforced polyaniline-dodecyl benzene sulfonate hydrogel with well-aligned fibrous morphology as durable electrode materials for Zn-ion battery

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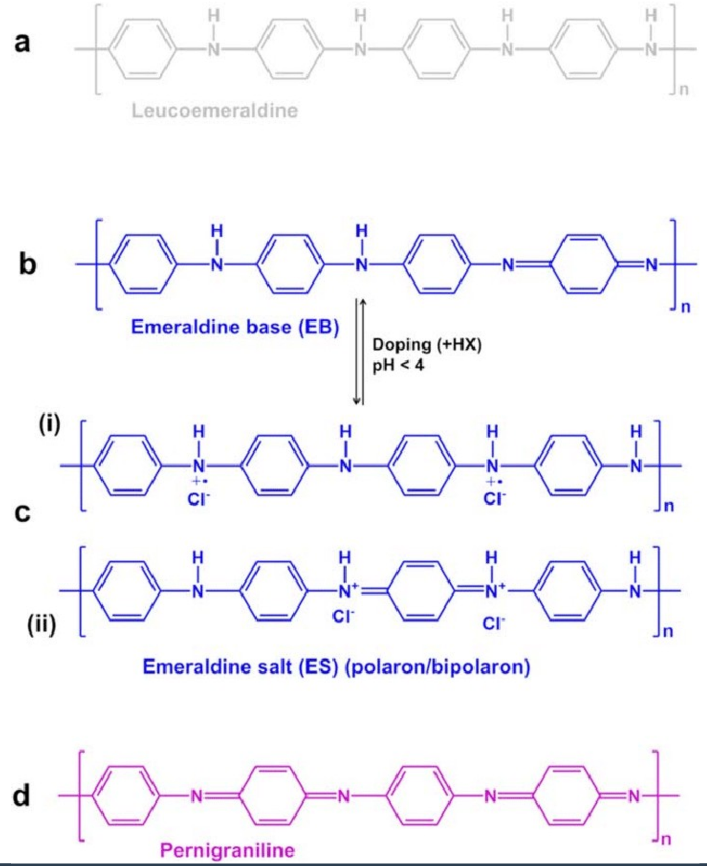
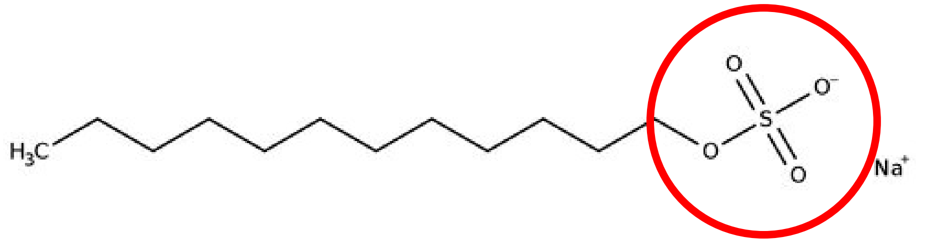
Introduction - Polyaniline

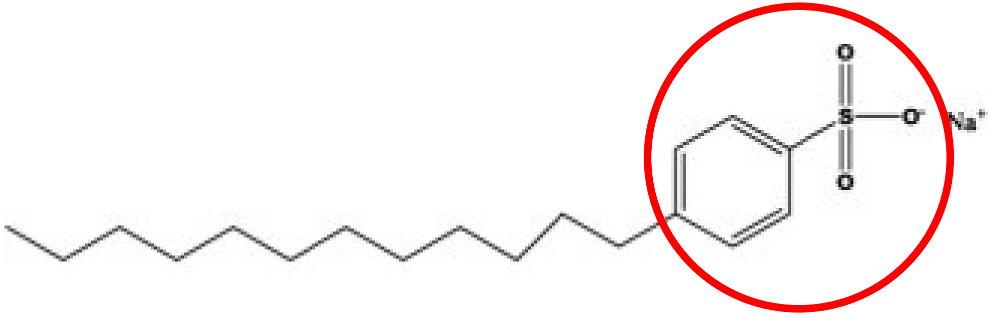
- Polyaniline is a semi-conductor polymer;
- We can easily change the amount of free charge in the chain.



Introduction - Surfactants

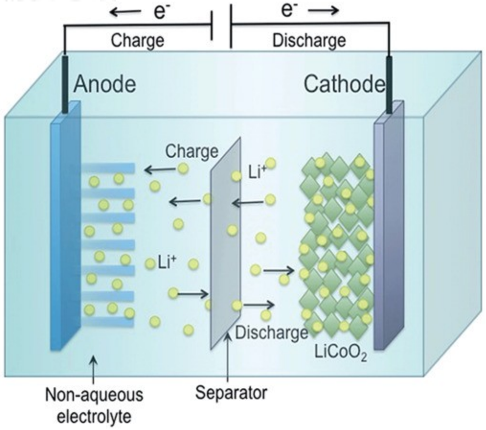
- **Sodium Dodecyl Sulfate (SDS):**
  - Anionic surfactant
  - Amphipilic molecule
- **Sodium Dodecyl Benzene Sulfonate (SDBS):**
  - Anionic surfactant
  - Amphipilic molecule





Introduction - Lithium-ion and Zn-ion battery

- High energy density, long service life and high energy efficiency, the LIB (lithium-ion battery) has become one of the most widely used electrochemical power sources. However toxicity, flammability and explosibility of the organic electrolytes, and restricted storage and high price of Li source is a problem with this battery.
- Using mild acidic aqueous solution of zinc salt (such as $ZnSO_4$) as electrolyte, the Zn-ion battery also possesses the advantages of low cost, safety, environmental friendliness, and high rate capacity.

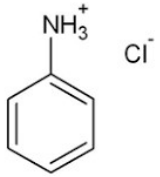


Objectives

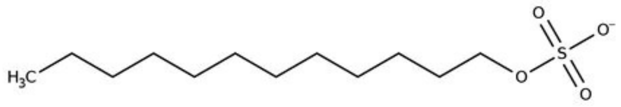
- Make a cathode for a Zn-ion battery using PANI-SDS, PANI-SDBS and PANI as the principal component.

Materials

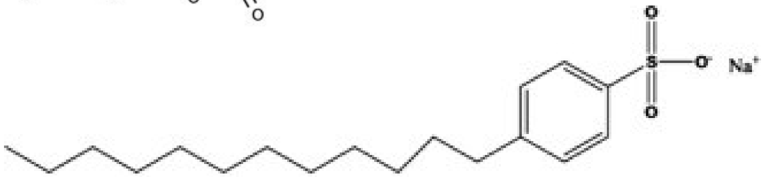
- **Aniline hydrochloric** →



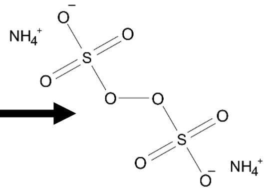
- **Sodium Dodecyl Sulfate** →



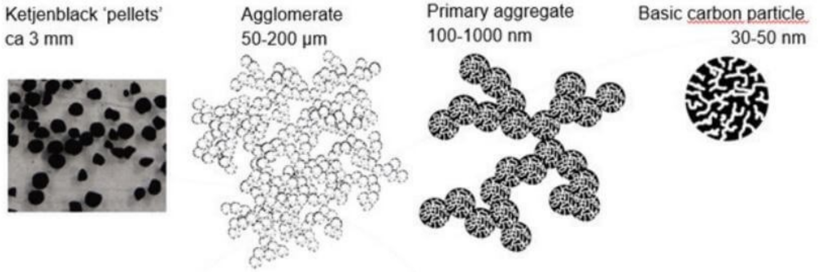
- **Sodium Dodecyl Benzene Sulfonate** →



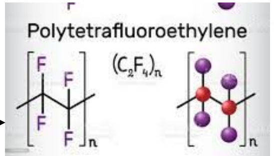
- **Ammonuim persulfate (APS)** →



- **Ketjenblace (Carbon Black)** →



- **Polytetrafluoroethylene (Teflon)** →



Synthesis of the conducting polymer hydrogels

- **The conducting polymer hydrogels were synthesized by a facile one-pot method.**

After dissolved all the components
[APS] = 3 mM was added

[SDBS] = 1 mM
or
[SDS] = 1 mM

[Aniline] = 3 mM

Stirring and in ice-water bath

After added APS, the mixture stay in intense agitation for 30 seconds and go to the refrigerator (~4 °C) for 12 hours.

Cathode electrode

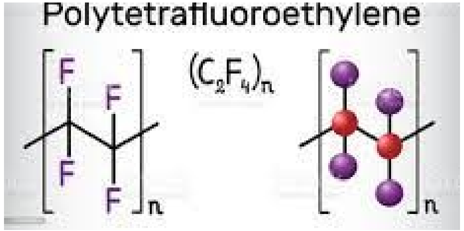
- **The freeze-dried powders of PANI-SDBS, PANI-SDS and PANI were used as active materials in electrodes for Zn-ion battery.**

PANI-SDBS/ PANI-SDS/PANI

powder

+

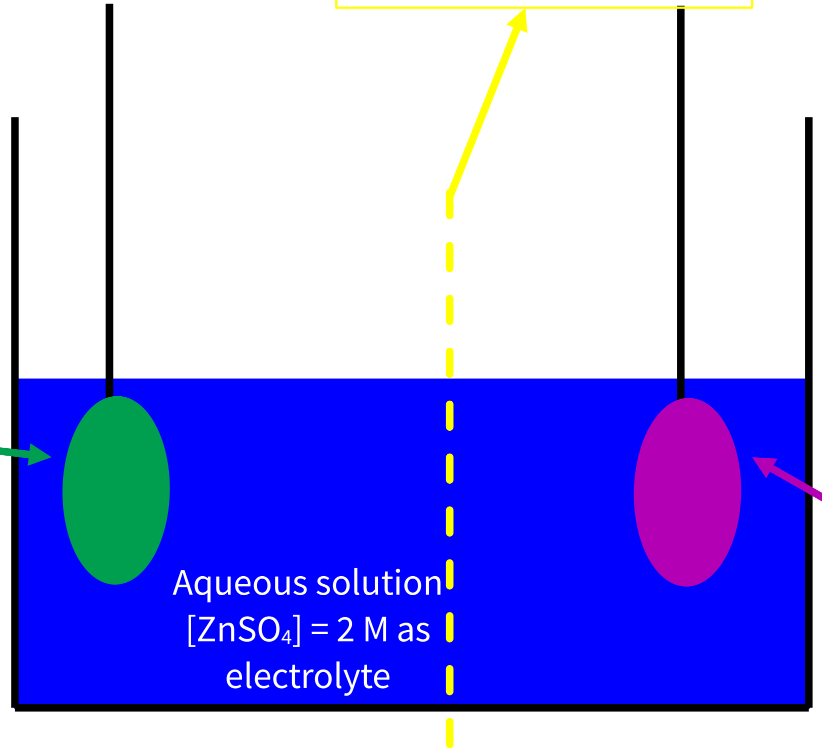
+

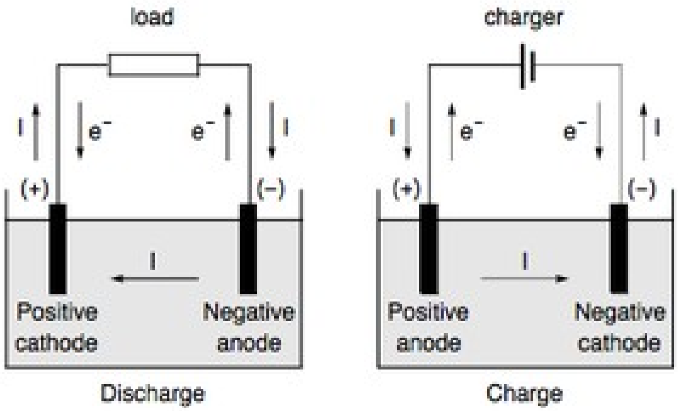


Mass ratio 8 – 1 – 1

- **This is mixture and pressed on the stainless mess collector created a thin film.**

Battery


Paper filter
Cathode electrode
(previous slide)
Aqueous solution
[$ZnSO_4$] = 2 M as
electrolyte
Zn foil
as anode


load
I
e⁻
(+)
(−)
Positive
cathode
Negative
anode
Discharge
charger
Positive
anode
Negative
cathode
Charge

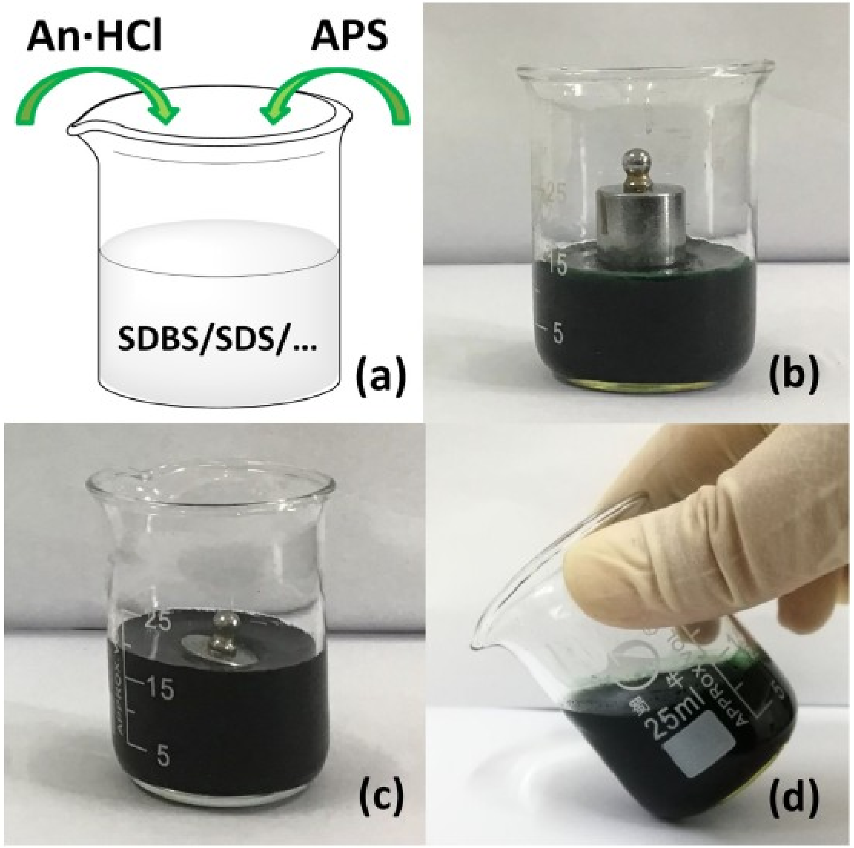
Characterization techniques

- Fourier transform infrared spectrometer (FT-IR);
- X-ray diffraction (XRD) ;
- Field-emission scanning electron microscope (FE-SEM).

Results – The synthesized of the conducting polymer hydrogels

Synthesis illustration

PANI-SDBS



The mechanical strenght for PANI-SDBS is more than PANI-SDS (metallic weight)

PANI-SDS

PANI

Results – The synthesized of the conducting polymer hydrogels

Table S1 Gelation test under various concentrations of the aniline hydrochloric salt for PANI-SDBS and PANI-SDS

Sample	Concentration of aniline hydrochloric salt (mol/L)	Gelation phenomenon	No.
PANI-SDBS	0.3	gel	1
	0.2	gel	2
	0.15	gel	3
	0.1	gel	4
	0.08	no gel	5
PANI-SDS	0.3	gel	6
	0.2	gel	7
	0.18	gel	8
	0.15	no gel	9

Note: the concentrations of SDBS and SDS used in PANI-SBDS and PANI-SDS are 0.1 mol/L. The molar ratios of aniline hydrochloric salt and ammonium persulfate (APS) in all samples are 1.

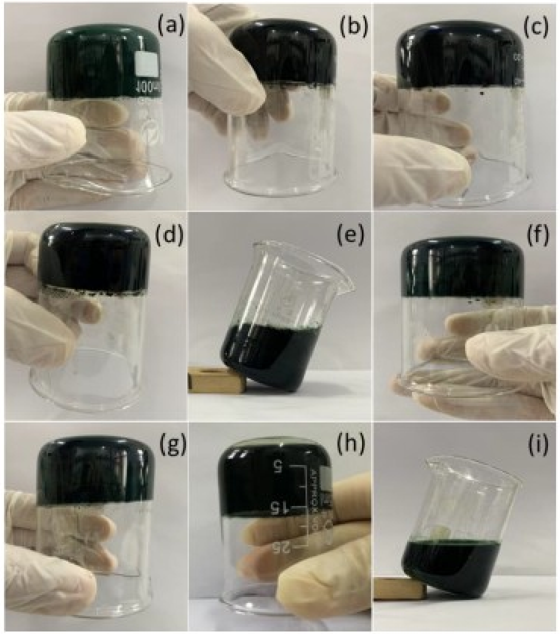


Fig. S1 Digital photos of samples in Table S1: 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), 6 (f), 7 (g), 8 (h), 9 (i).

Results - FT-IR

- PANI:
  - 1585 cm^{-1} C=C stretching vibrations of the quinonoid ring
  - 1499 cm^{-1} C=C stretching vibrations of the benzenoid ring
  - 1304 cm^{-1} C–N stretching
  - 1144 cm^{-1} C=N stretching
- PANI-SDS and PANI-SDBS:
  - 1585 cm^{-1} and 1144 cm^{-1} shifted to lower wavenumbers.

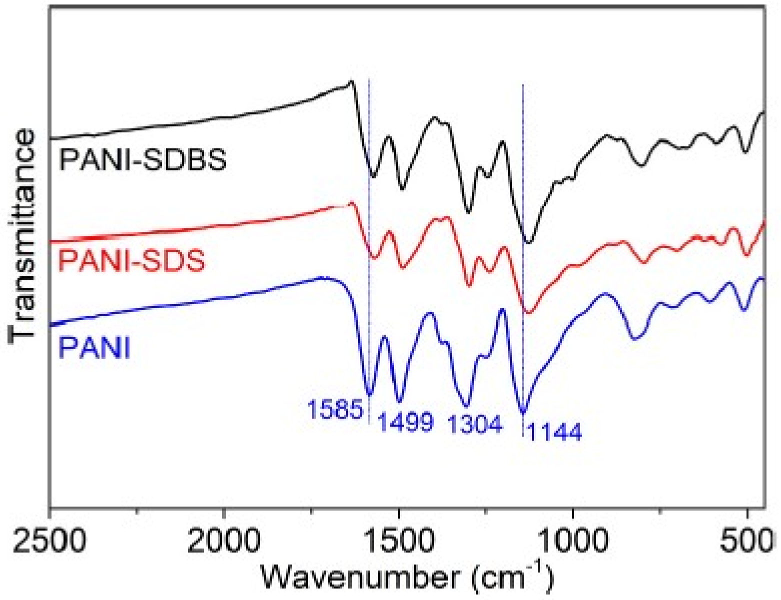
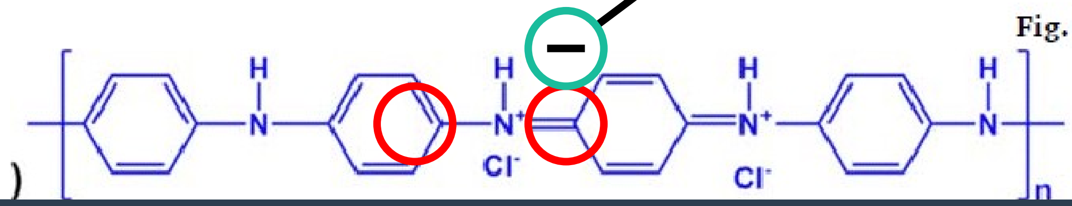


Fig. 2. FI-IR spectra of PANI-SDBS, PANI-SDS and PANI.



Results - XRD

- $2\theta = 19.8$ parallel periodicity to the PANI chains.
- $2\theta = 25.2$ perpendicular periodicity to the PANI chains.

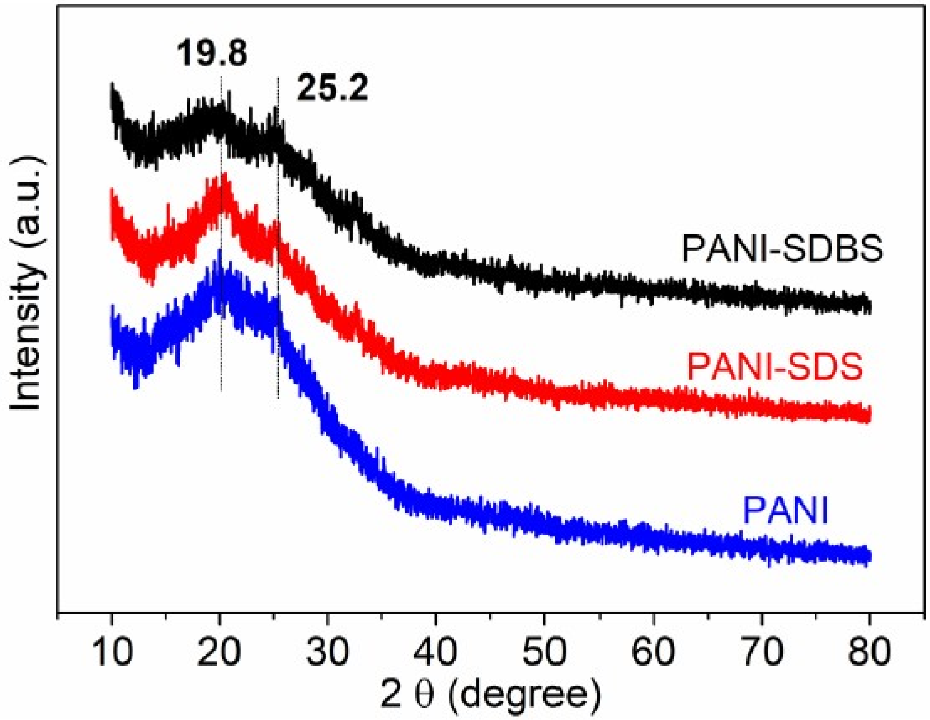
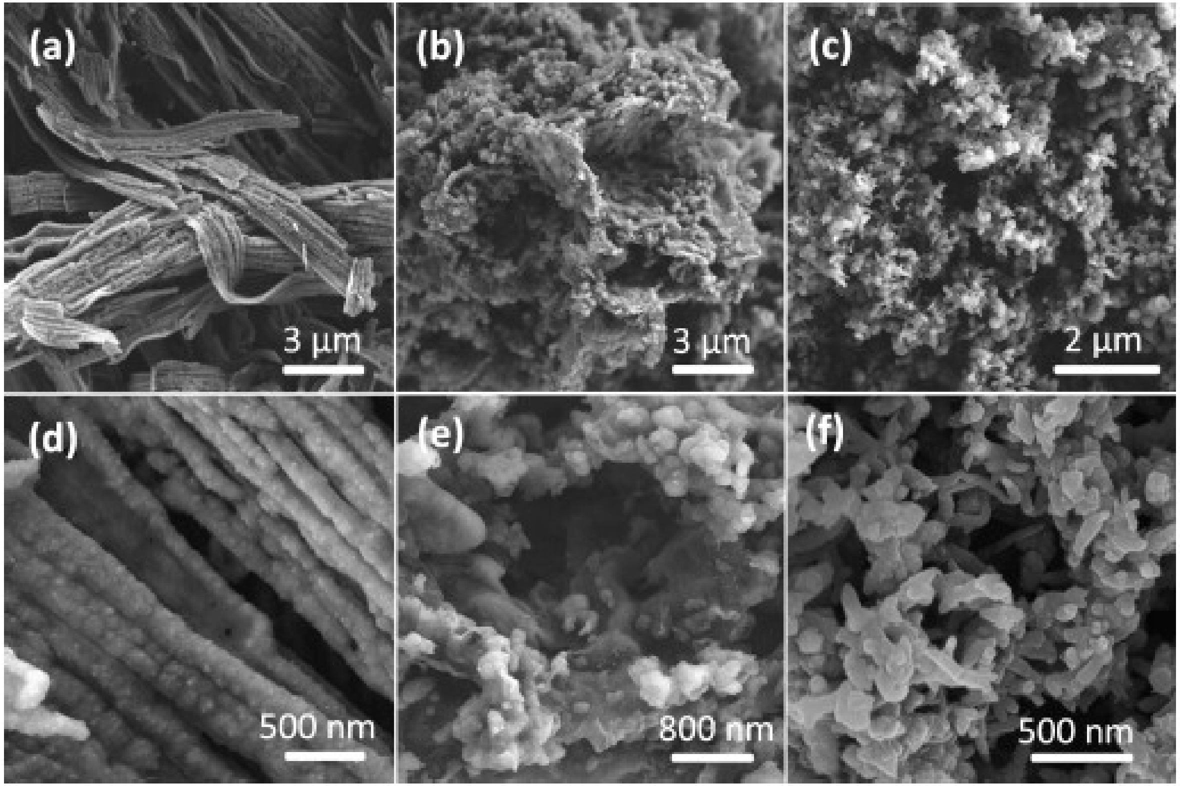


Fig. S2 XRD patterns of PANI-SDBS, PANI-SDS and PANI.

Results - FE-SEM

- PANI-SDBS form nanorods with 200 nm diameter and some microns in lenght.
- PANI-SDS form aggregates the nanoparticles.
- Because this form hydrogels and The mechanical strenght for PANI-SDBS is more than PANI-SDS.

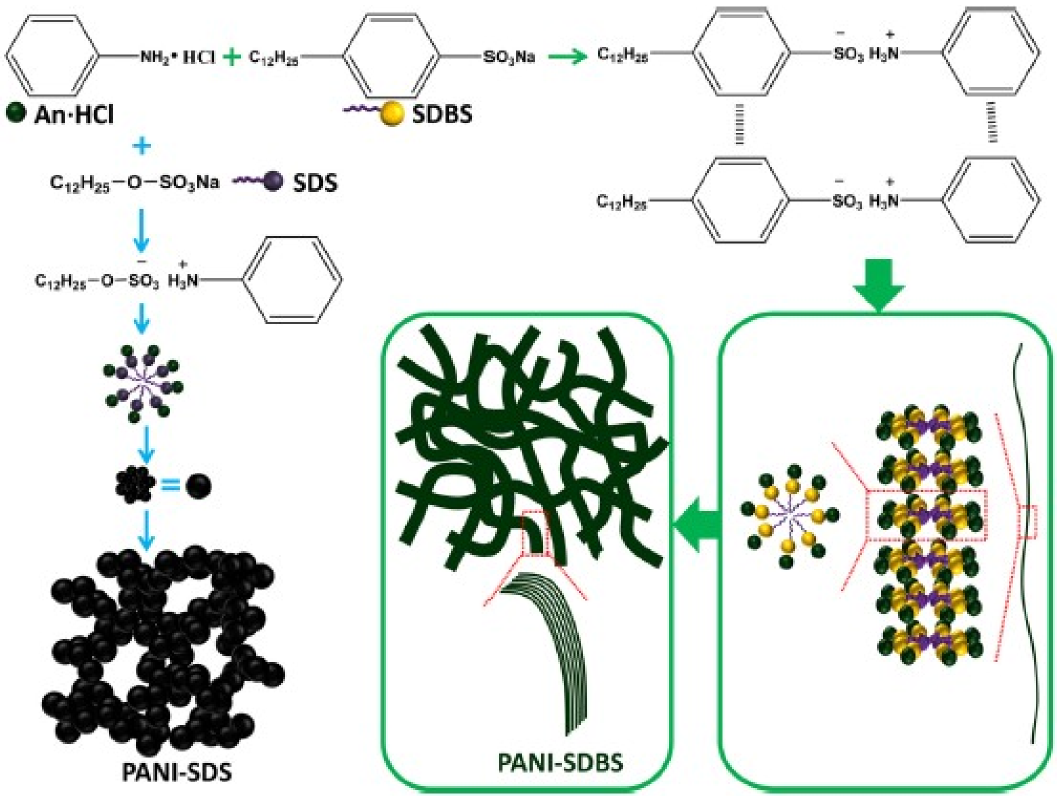


PANI-SDBS PANI-SDS PANI

Results – Propostal for the mechanism formation

- Surfactant electrostatic interaction with aniline hydrochloric.

- SDBS because the benzene ring form π-π stacking in the vertical direction.



Results

Because the plateus (d) is more distinct in PANI-SDS and PANI-SDBS suggesting superior doping/dedoping. The 3D structure is more efficient for charge transportation than just the polymer.

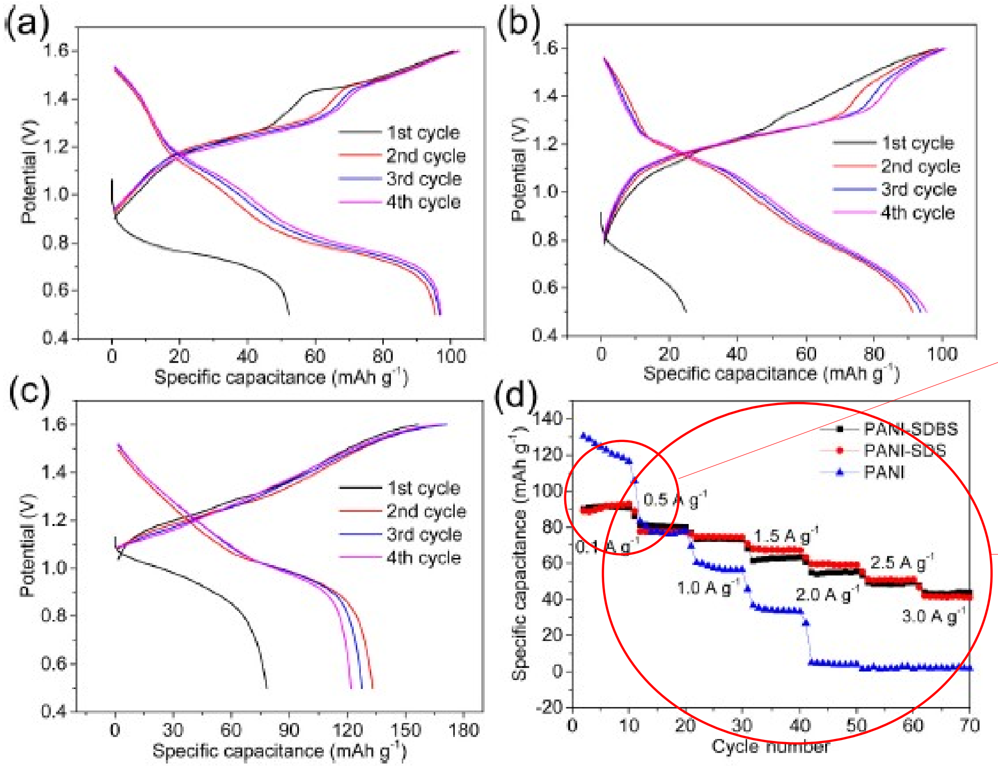


Fig. 5. Electrochemical performance of PANI-SDBS, PANI-SDS and PANI cathodes in Zn-ion batteries: the initial GCD profiles of PANI-SDBS (a), PANI-SDS (b) and PANI (c), and their rate performance (d).

This difference is because SDBS and SDS is non-activity in the conduction

SDBS and SDS make the electrode more stable.

Results

- Initially PANI is more efficient than PANI-SDBS and PANI-SDS.
- After 20 cycles PANI eletrode was destroyed.
- PANI-SDBS after 1500 cycles has capacity retentions is 81.7% and PANI-SDS after 1500 cycles has capacity retentions is 44.4%.

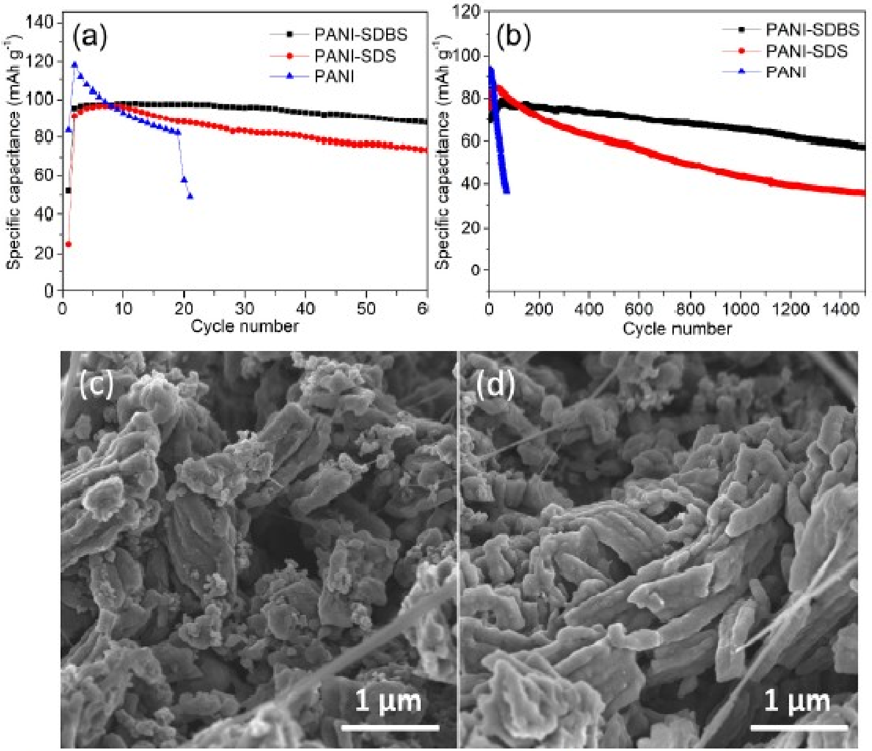


Fig. 6. Cycling stability during discharge/charge processes measured at current densities of 0.1 A g^{-1} (a) and 0.5 A g^{-1} (b). SEM images of the PANI-SDBS electrode before (c) and after (d) discharge/charge cycles.

Results

Table S2 Comparison of the cycling stability of PANI-SBDS and previously reported cathode materials for Zn-ion battery.

Sample	Retention (%) (number of cycles, current density)	Ref.
highly crystalline ramsdellite	65% (1000 cycles, 0.1 A g^{-1})	[1]
α-MnO_2 nanofiber	92% (5000 cycles, 1.54 A g^{-1})	[2]
naphthalenetetracarboxylic dianhydride	73.7% (2000 cycles, 1.0 A g^{-1})	[3]
layered $H_2V_3O_8$ nanowire	1000 (94.3%), 5 A g^{-1}	[4]
pyrene-4,5,9,10-tetraone	1000 (70%), 3 A g^{-1}	[5]
tetrachloro-1,4-benzoquinone	200 (70.3%), 0.217 A g^{-1}	[6]
VS_4@rGO nanocomposite	165 (93.3%), 1 A g^{-1}	[7]
MoS_2 nanosheets	1000 (87.8%), 1 A g^{-1}	[8]
bilayered $V_2O_5 \cdot nH_2O$	900 (71%), 6 A g-1	[9]
nanostructured $NiCo_2O_4$	1000 (62.23%), 1.0 A g^{-1}	[10]
polyaniline−cellulose Papers	84.7% (1000, 4.0 A g^{-1})	[11]
polypyrrole composite aerogels	80.3 % (1000 cycles, 2.0 A g^{-1})	[12]
PANI-SDBS (this work)	**81.7% (1500 cycles, 0.5 A g^{-1})**	

Conclusion

- The observation of FE-SEM shows that the microstructure of hydrogel is the typical 3D intertwined nanoribbons formed by well-aligned nanofibers, leading to the reinforced mechanical strength.
- The prepared PANI-SDBS hydrogel could be employed as the electrode materials for Zn-ion battery, and the electrochemical performance was evaluated by GCD test.
- As a result, the PANI-SDBS cathode exhibited favorable doping/dedoping kinetics and rate performance. More importantly, it delivered outstanding capacity retention (81.7%) after 1500 discharge/charge cycles at 0.5 A g^{-1}, which should be attributed to its well-aligned fibrous morphology.
- This PANI-SDBS hydrogel would be expected to have bright potential in durable cathode for Zn-ion battery.

Thank you