Electrochemical deposition of leaf stalk-shaped polyaniline doped with sodium dodecyl sulfate on aluminum and its use as a novel type of current collector in lithium ion batteries

Kairon Márcio de Oliveira

Index

- Introduction
- Objectives
- Reagents and materials
- Synthesis
- Preparation of SDS-PANI film onto the surface of a Al foil
- Preparation of novel current collector supported $LiFePO_4$ electrode
- Equipment used
- Results
- Conclusion

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Electrochemical deposition of leaf stalk-shaped polyaniline doped with sodium dodecyl sulfate on aluminum and its use as a novel type of current collector in lithium ion batteries

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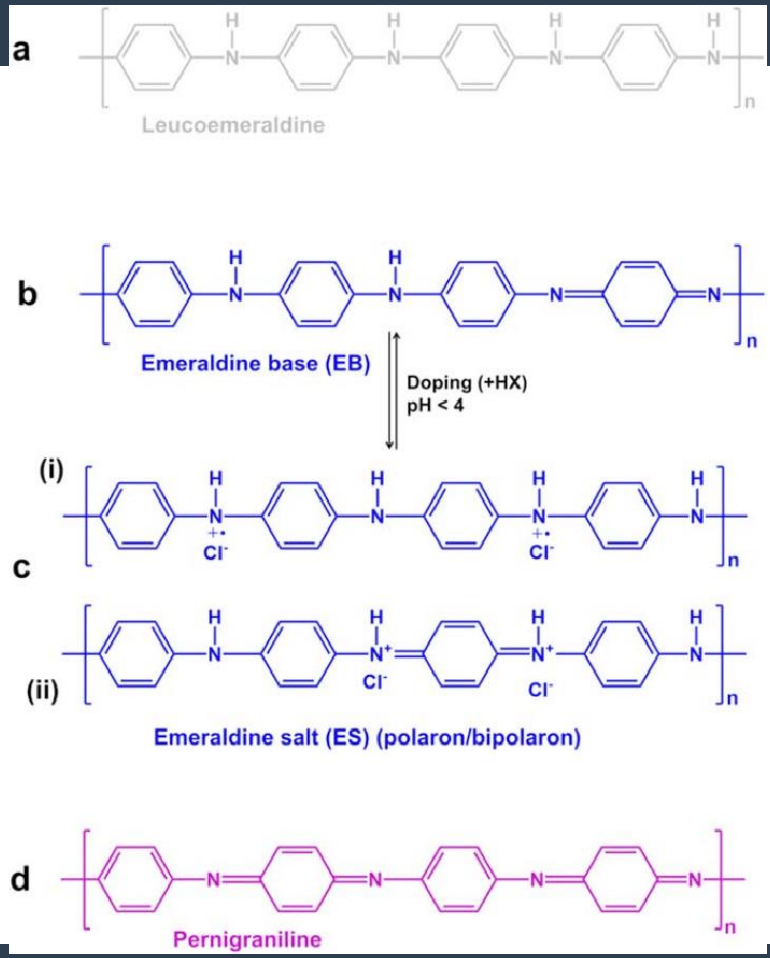
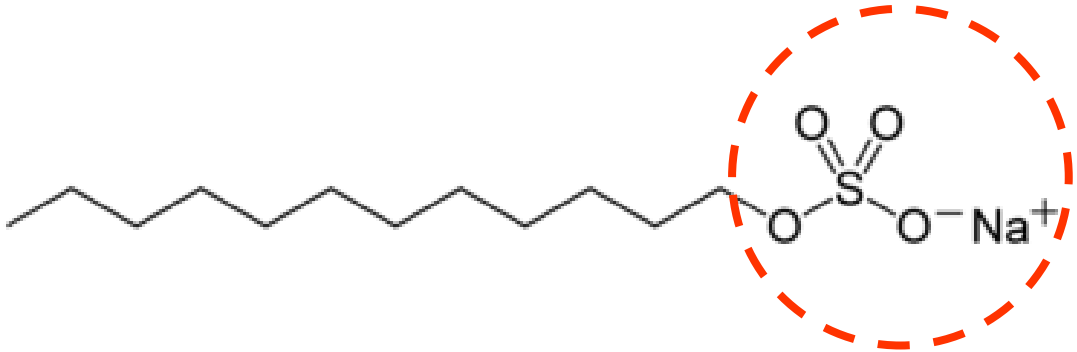
Introduction - Polyaniline

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

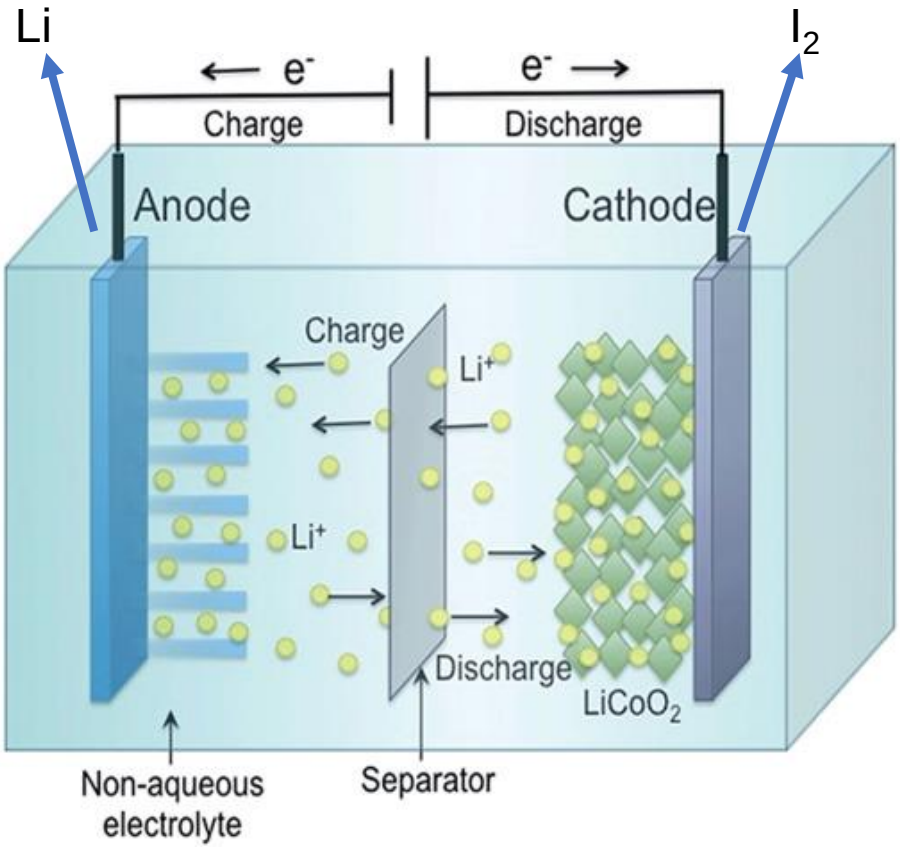


Introduction - Surfactant

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



Introduction



Example:

- Anode reaction: $2\ Li_{(s)} \rightarrow 2\ Li^{+}_{(s)} + 2e^{-}$
- Cathode reaction: $1\ I_{2(s)} + 2e^{-} \rightarrow 2\ I^{-}_{(s)}$
- Global reaction: $2\ Li_{(s)} + 1\ I_{2(s)} \rightarrow 2\ LiI_{(s)}$

Objectives

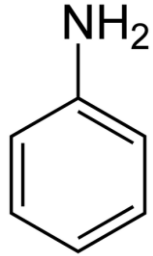
- **Synthesis and characterization of the SDS-doped PANI films onto the surface of a commercial aluminum foil through cyclic voltammetry**
- **Product electrode with commercial $LiFePO_4$ for studied the charge-discharge comportment.**

Reagents and materials

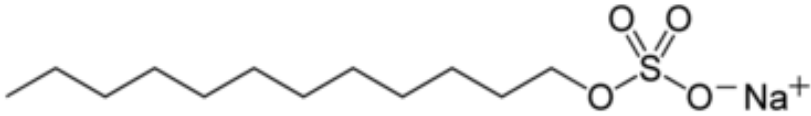
- Aniline
- Sodium Dodecyl Sulfate (SDS)
- Sulfuric acid (H_2SO_4)
- Aluminum foil (Al)
- $LiFePO_4$
- Acetylene black
- Polyvinylidene fluoride
- LiPF6 electrolyte

Reagents and materials

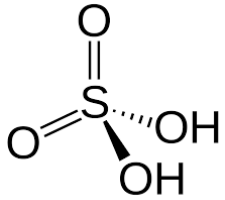
- **Aniline**



- **Sodium Dodecyl Sulfate (SDS)**



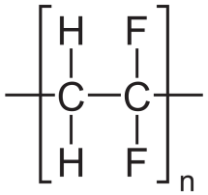
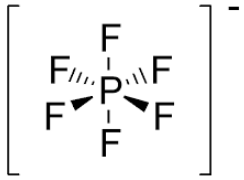
- **Sulfuric acid (H_2SO_4)**



- **Aluminum foil (Al)**

Commercial

Reagents and materials

- $LiFePO_4$ (LFP) →  Commercial
- Acetylene black (conductive carbon black) → 
- Polyvinylidene fluoride →  
- $LiPF_6$ electrolyte → Li^+ 

Preparation of SDS-PANI film onto the surface of a Al foil

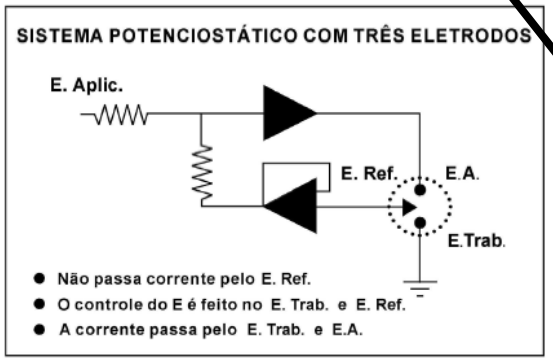
H2SO4 (0.5 M)

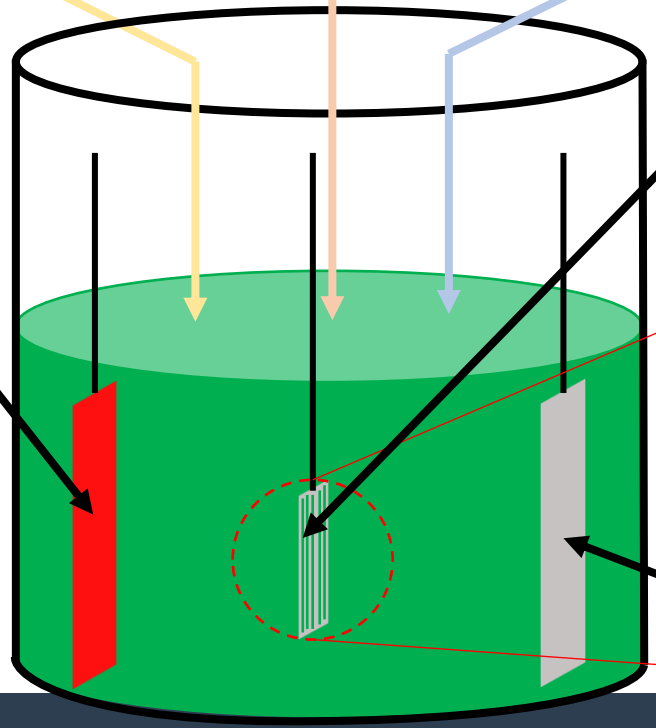
Aniline (0.4 M)

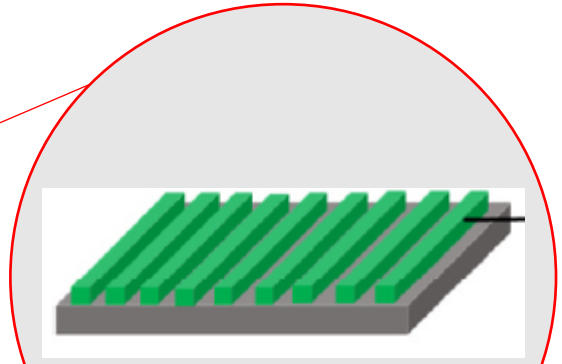
SDS (2 mM)

Saturated calomel electrode (SCE) (reference electrode)

Al foil (working electrode)





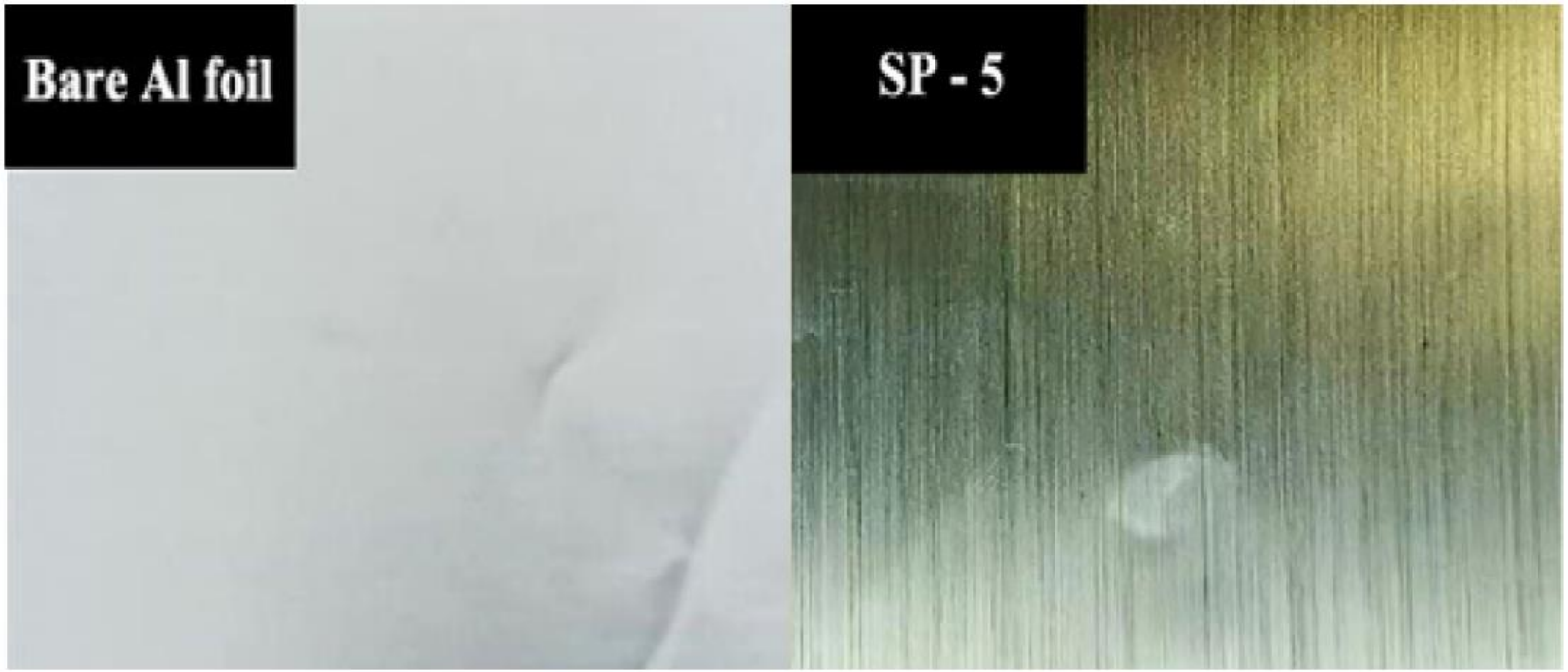


Platinum foil were (counter electrode)

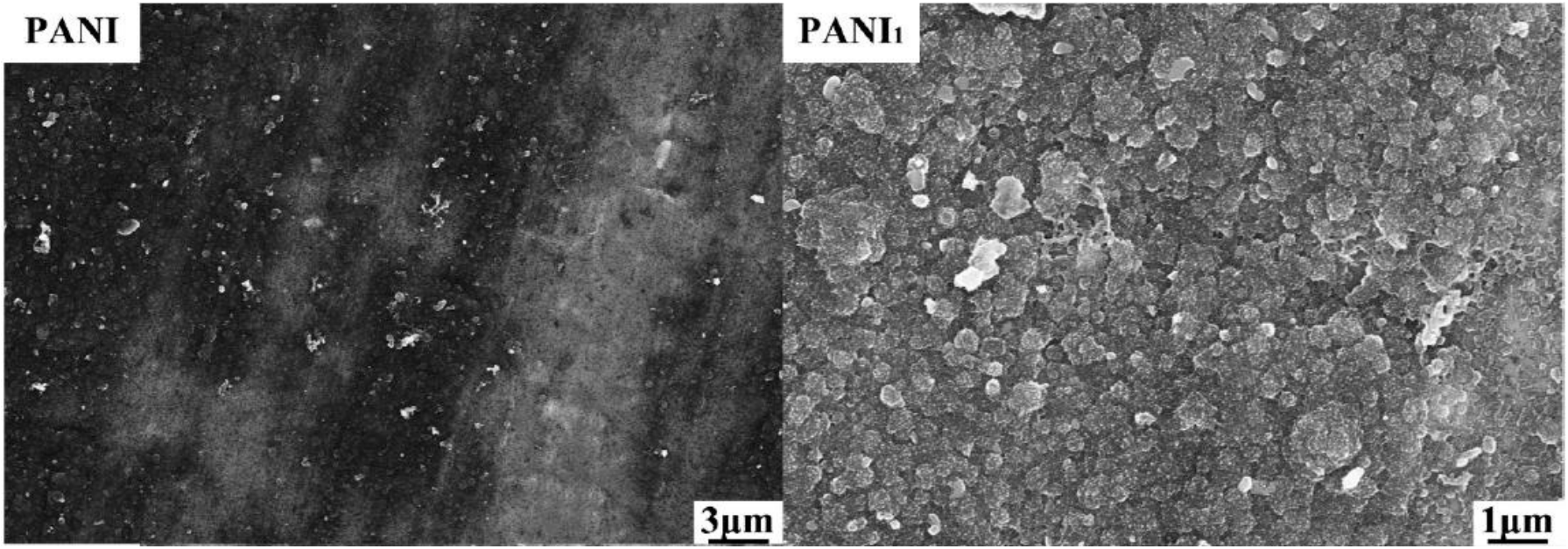
Equipment used

- Scanning electron microscopy (SEM)
- Fourier-transform infrared spectrometry (FTIR)
- X-ray diffraction (XRD)
- Raman spectroscopy

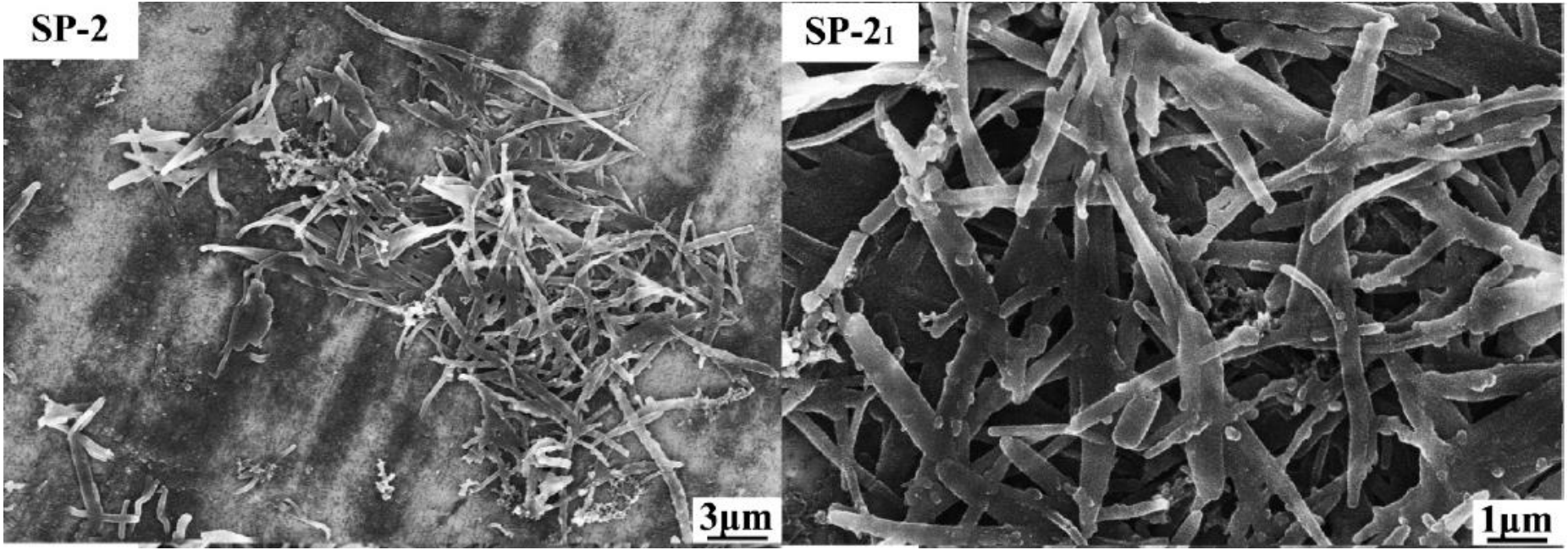
Results – Images



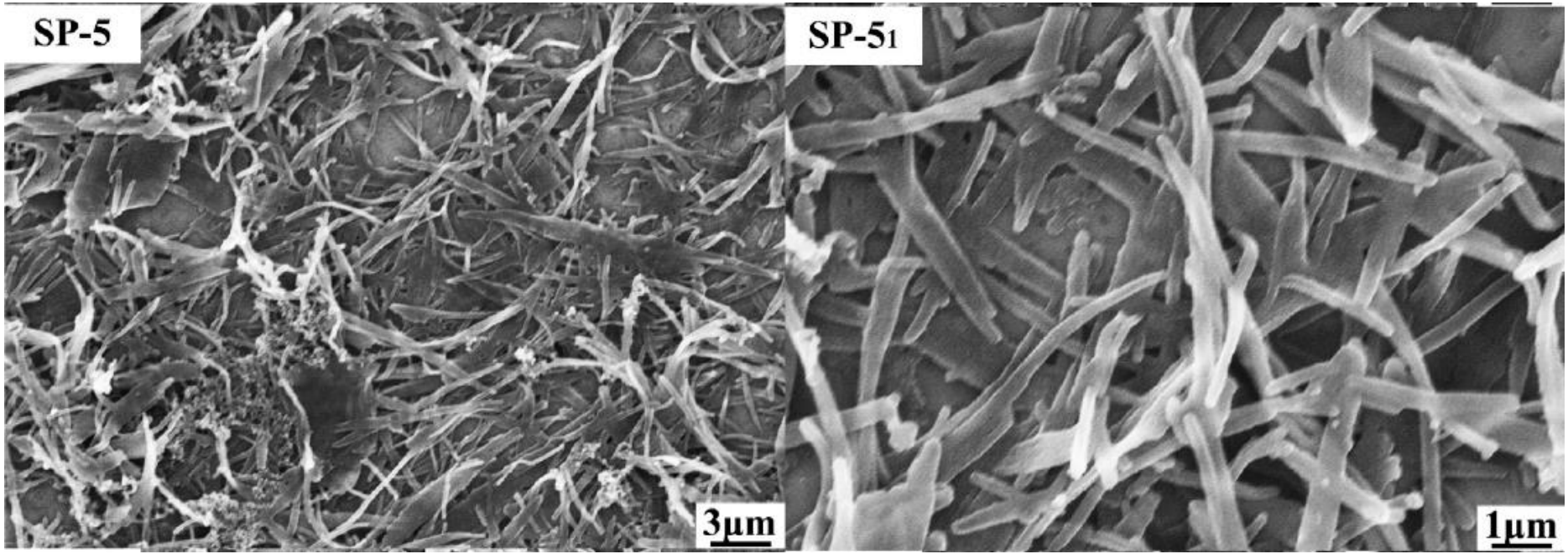
Results – SEM images



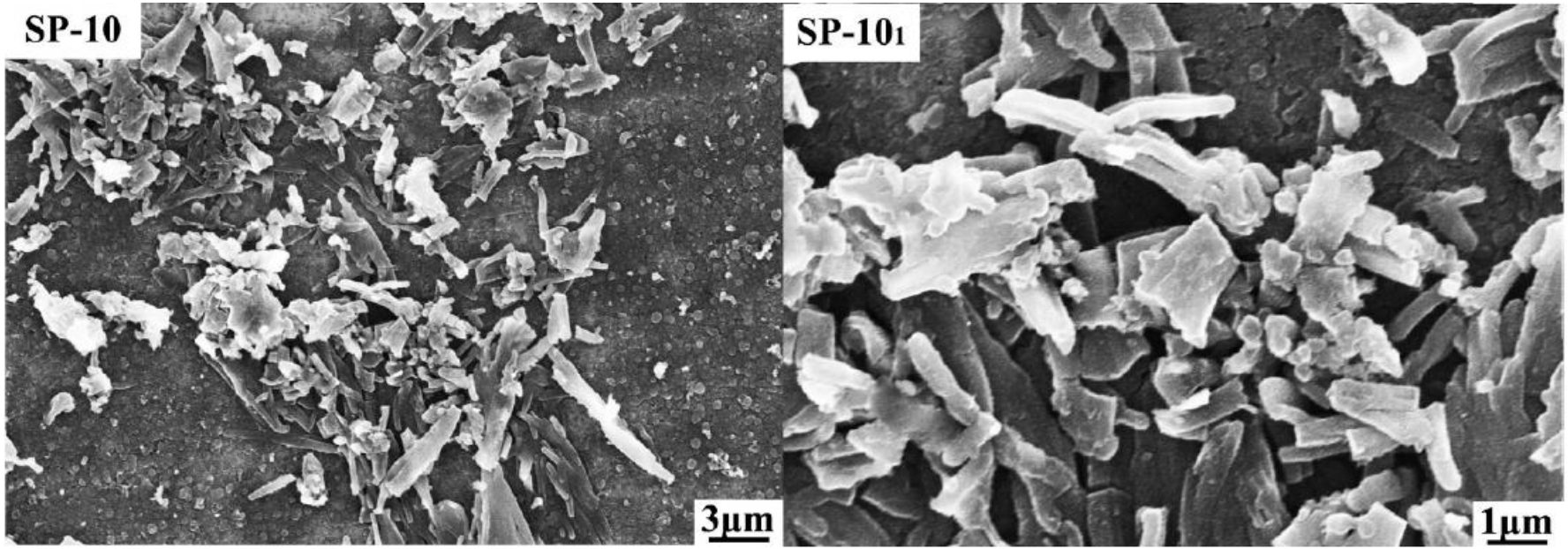
Results – SEM images



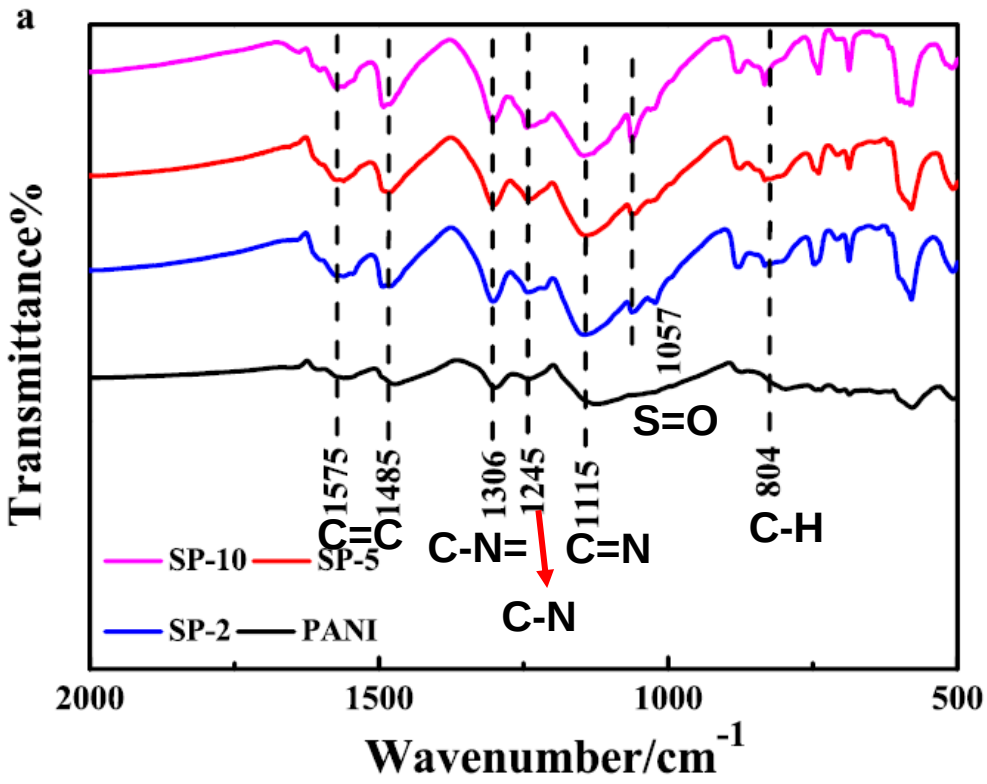
Results – SEM images

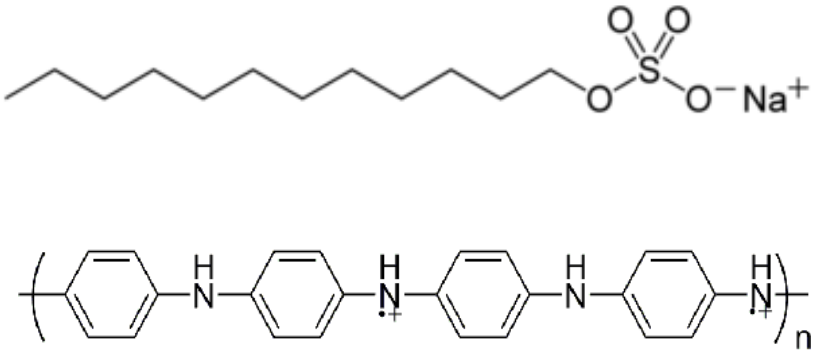


Results – SEM images



Results – FTIR spectra



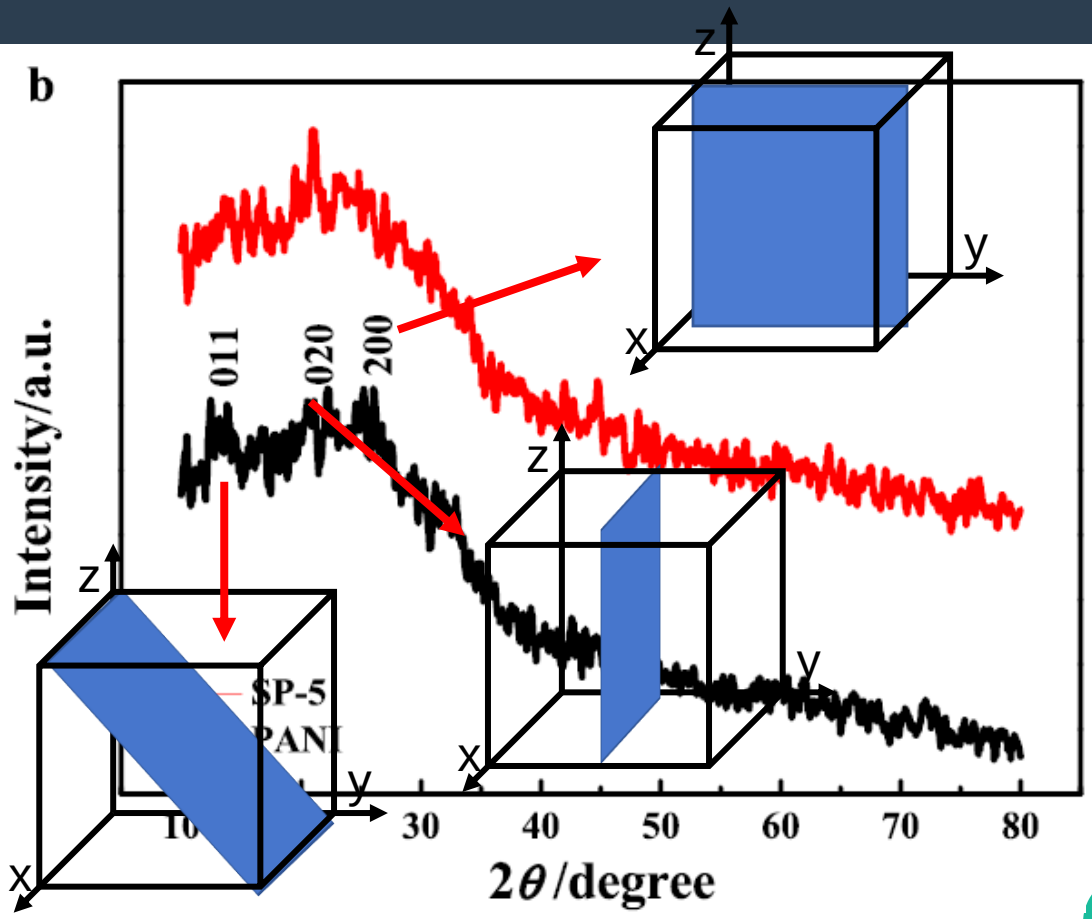


Polyaniline (Emeraldine Salt)

Indicating that the contents of the PANI functional groups were greatly increased due to the addition of SDS in the electrolyte solution

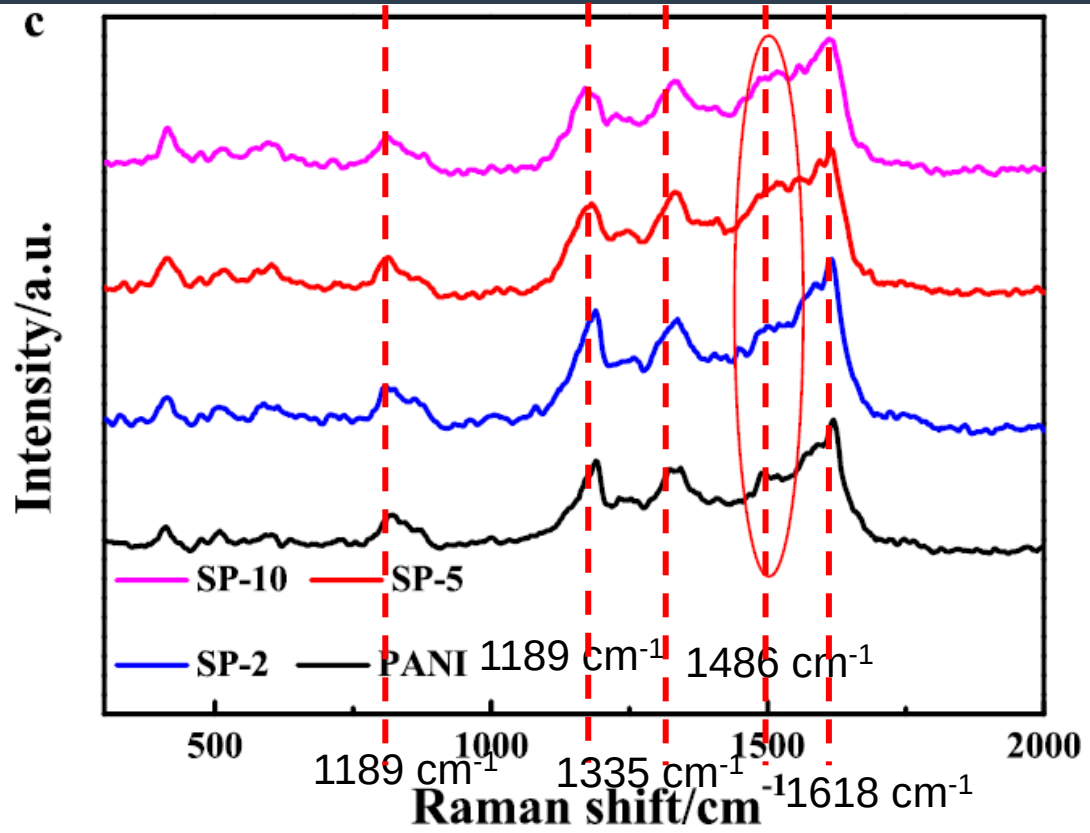
Results – XRD patterns

- Indicating the successful preparation of emeraldine salt of PANI.
- The presence of the sharp diffraction peak at 20.7◦ effectively indicated that the crystallinity of PANI in SP-5/Al was superior to that of PANI in P/Al .



Results – Raman spectra

- The peaks located at 1618, 1486, 1335, 1189 and 817 cm^{-1}, suggesting that the prepared film was a PANI film.
- 1486 cm^{-1} became weaker, which indicated that the amounts of C=N quinoid in the prepared films decreased evidently due to the presence of SDS.



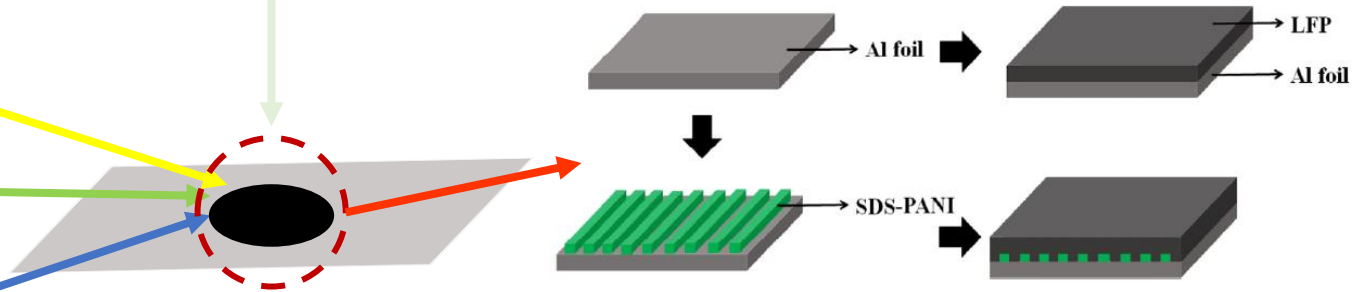
Preparation of novel current collector supported $LiFePO_4$ electrode

40 drops of N-methylpyrrolidone (NMP)

8 LFP (0.3 g)

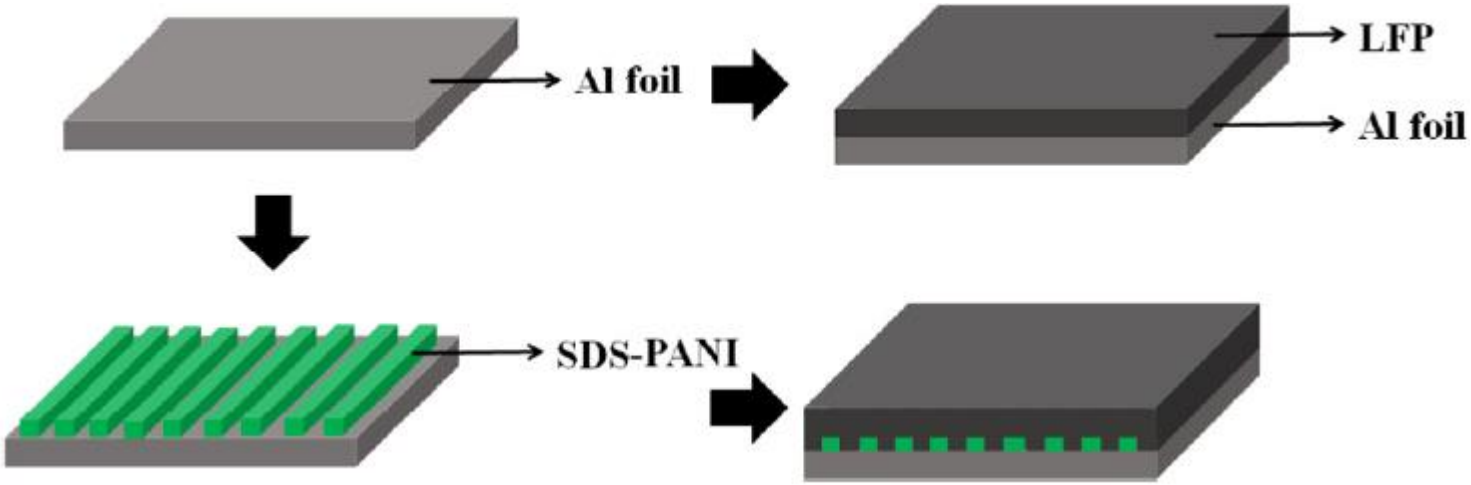
1 Polyvinylidene fluoride (PVDF) (0.0375 g)

1 Acetylene black (0.0375 g)



The mixed solvent containing dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC) and vinylene carbonate (VC) was used as the organic solvent to dissolve LiPF6 forming an organic electrolyte.

Difference between the electrodes



Equipment used

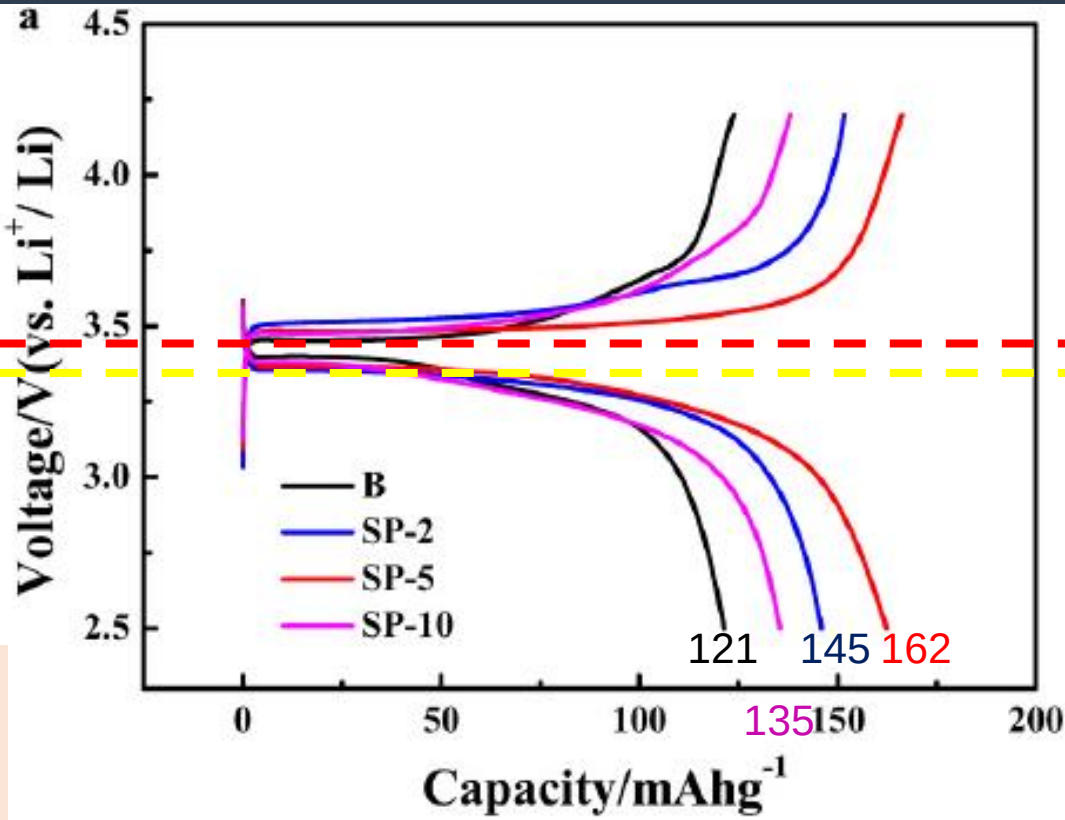
- **Galvanostatic charge and discharge (Potential between 2.5 V to 4.2 V, and current rates were 0.2 C, 0.5 C, 1 C and 5 C (For $LiFePO_4$, 1 C = 170 $mAhg^{-1}$))**

- **The electrochemical impedance spectroscopy (EIS)**

Results – Charge–discharge profiles and Cycling performances

Attributed to the following electrochemical reaction ($LiFePO_4 \rightarrow FePO_4 + Li^+ + e^-$) exhibiting an anodic electro-oxidation process

The contrary electro-reduction process, as displayed by the voltage plateau appearing at about 3.38 V, occurred in discharge process.

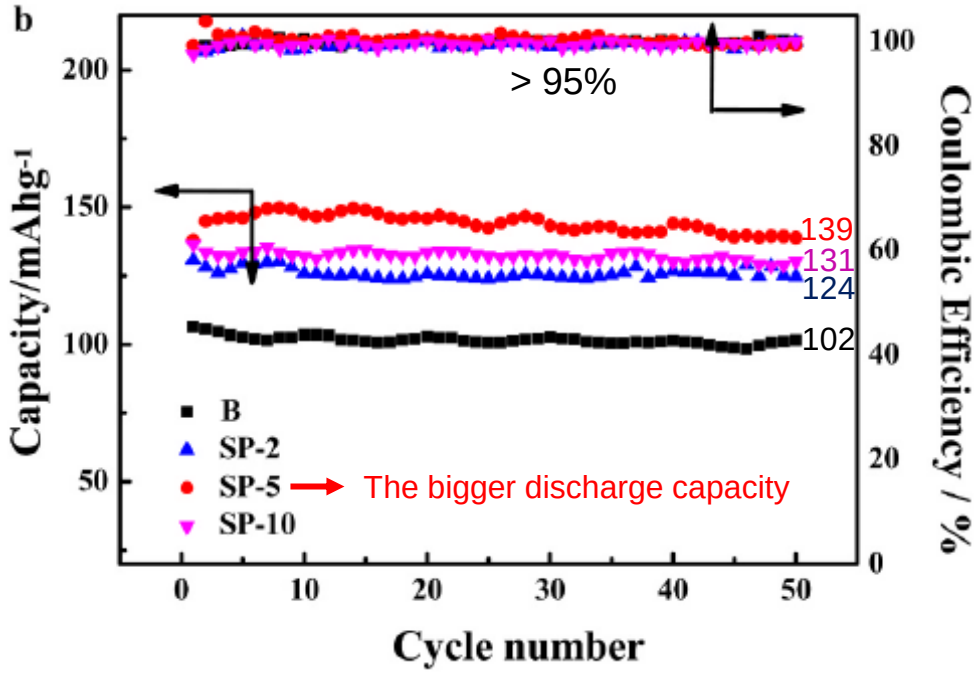


The LFP on the SP modified had a promotional effect of the discharge capacity pf LFP

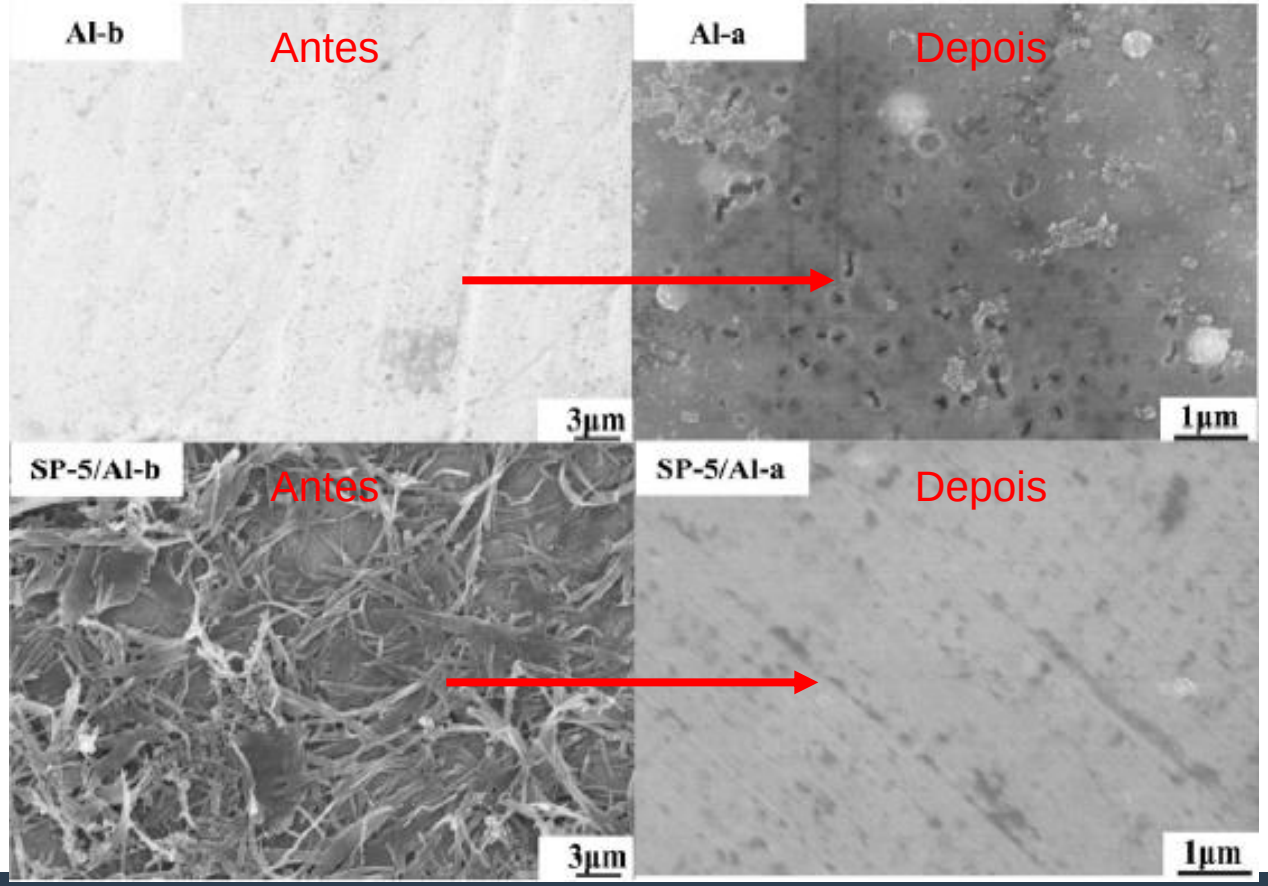
Results – Charge–discharge profiles and Cycling perfirmances

- **Conditions for the experiment: 0.5 C for 50 cycles.**

- **The electrode assembled using current collector SP-5/Al delivered the best cycling performance among all investigated electrodes.**

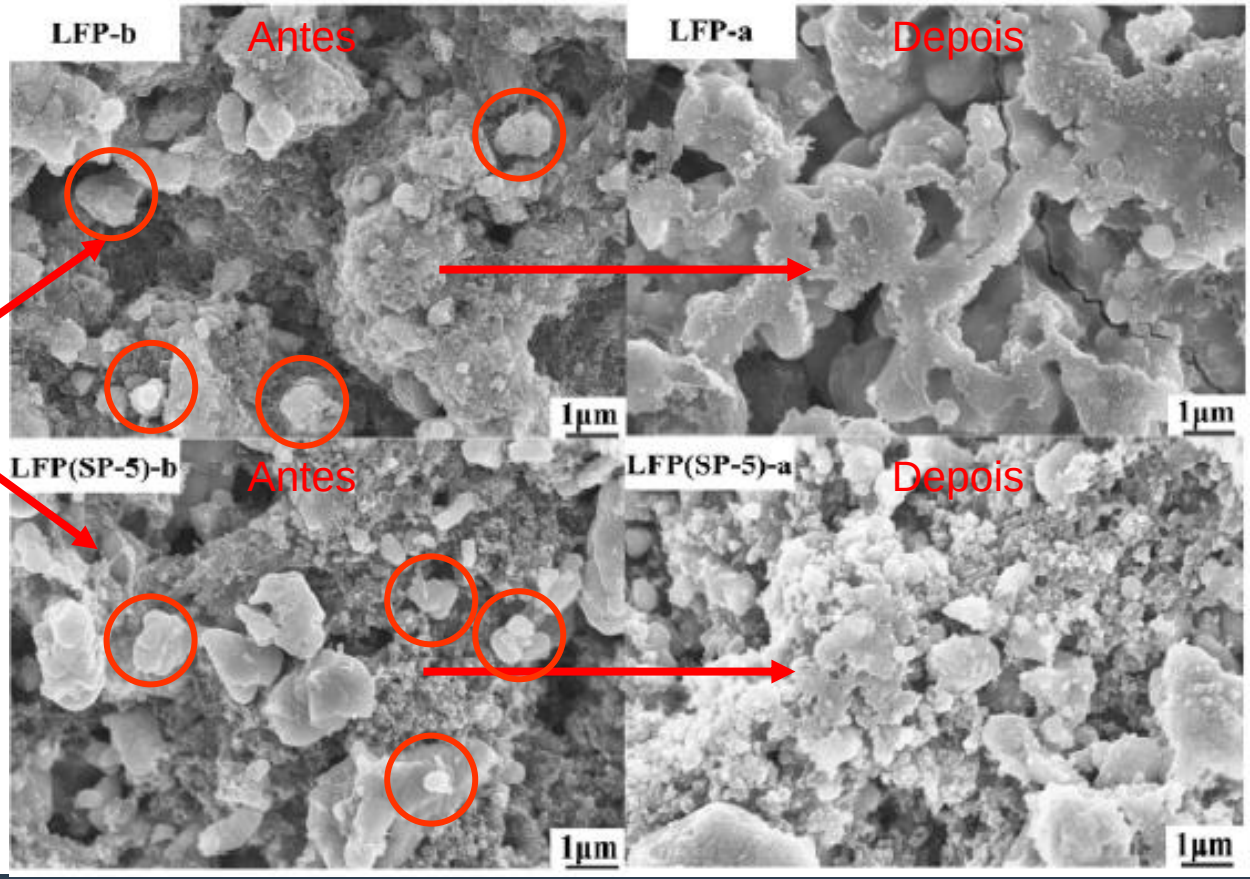


Results – SEM images



Corrosion process of Al foil was greatly inhibited by the presence of SP-5 film on the surface of Al foil.

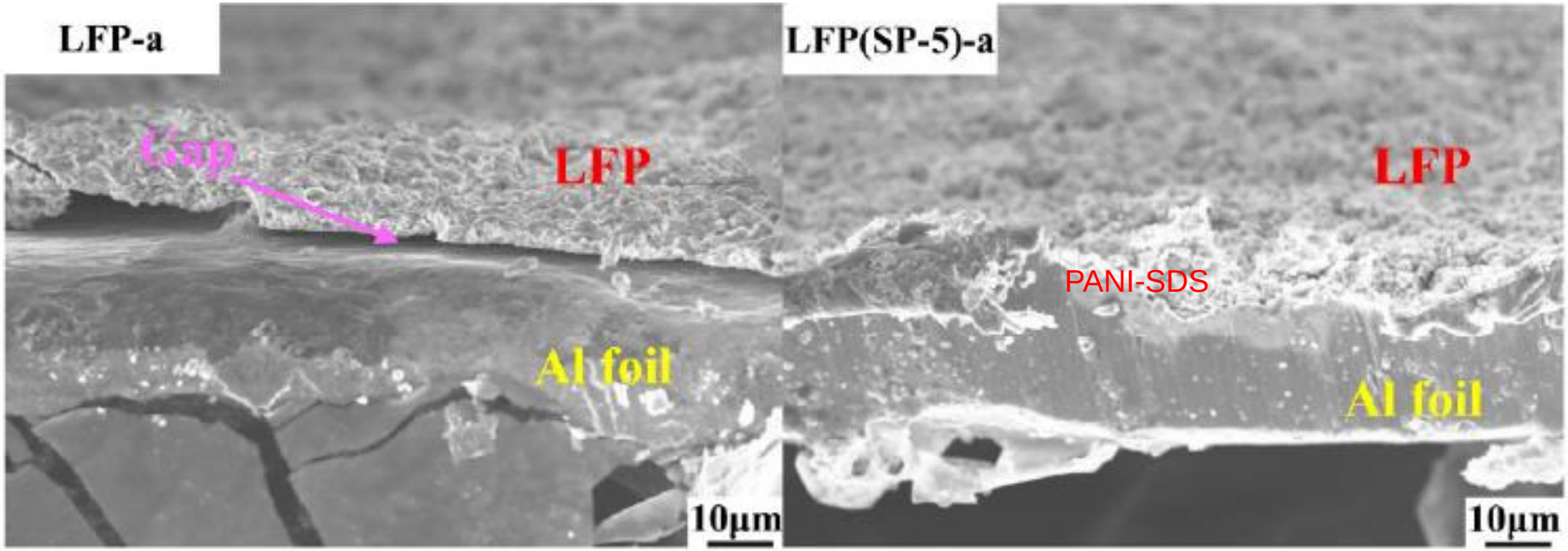
Results – SEM images



Small irregular particles

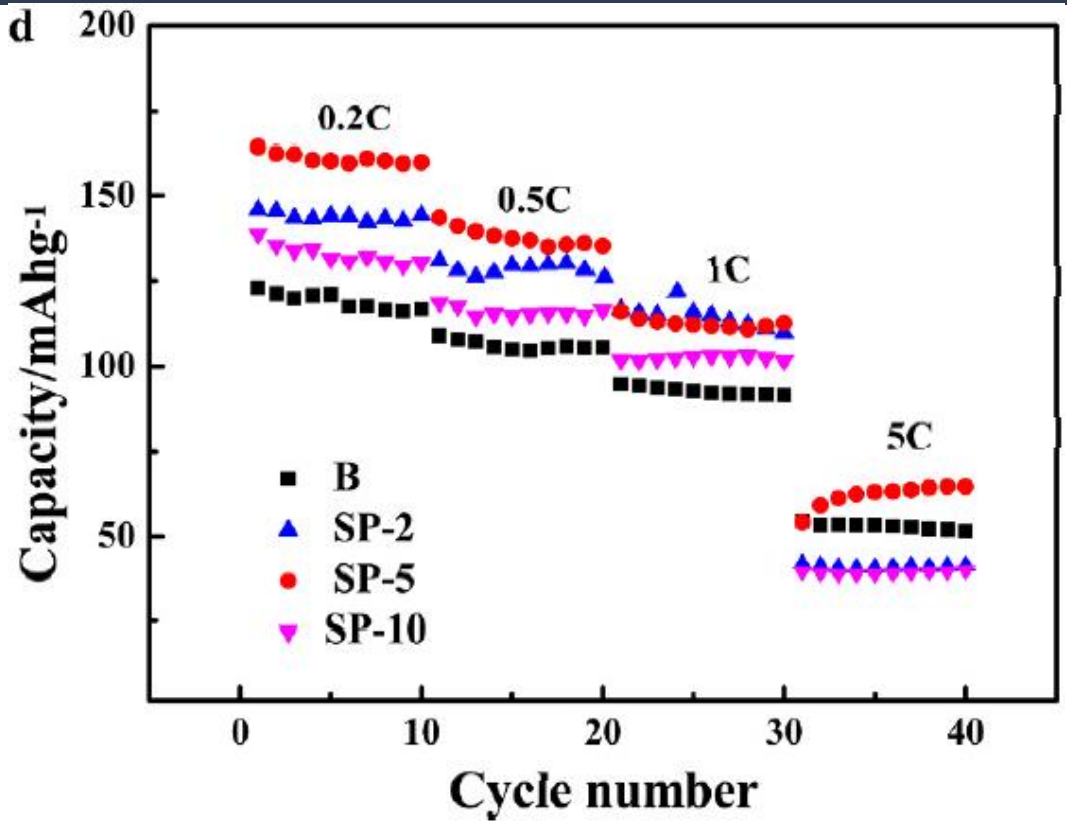
Results – SEM images

Very beneficial to the transfer process of both electrons and lithium ions



Results – Rate capabilities

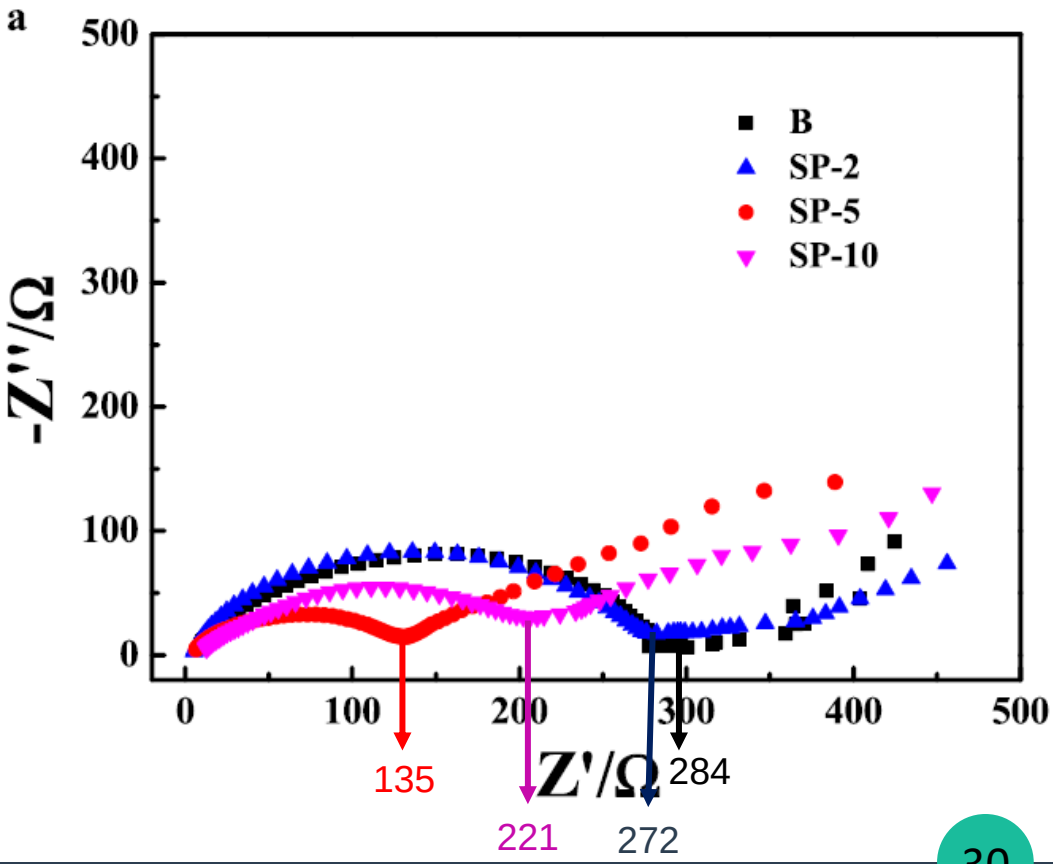
The improvement of LFP discharge capacity was of great significance since LFP was one of the most widely commercialized cathode materials, to our knowledge, owing to its reliable security and low cost as well as the satisfied electrochemical performance.



Results – Nyquist plots

- The diameter of the semicircle is approximately the value of the charge transfer resistance (Rct).
- The smaller value of (Rct) signified a faster kinetics of lithium ions.

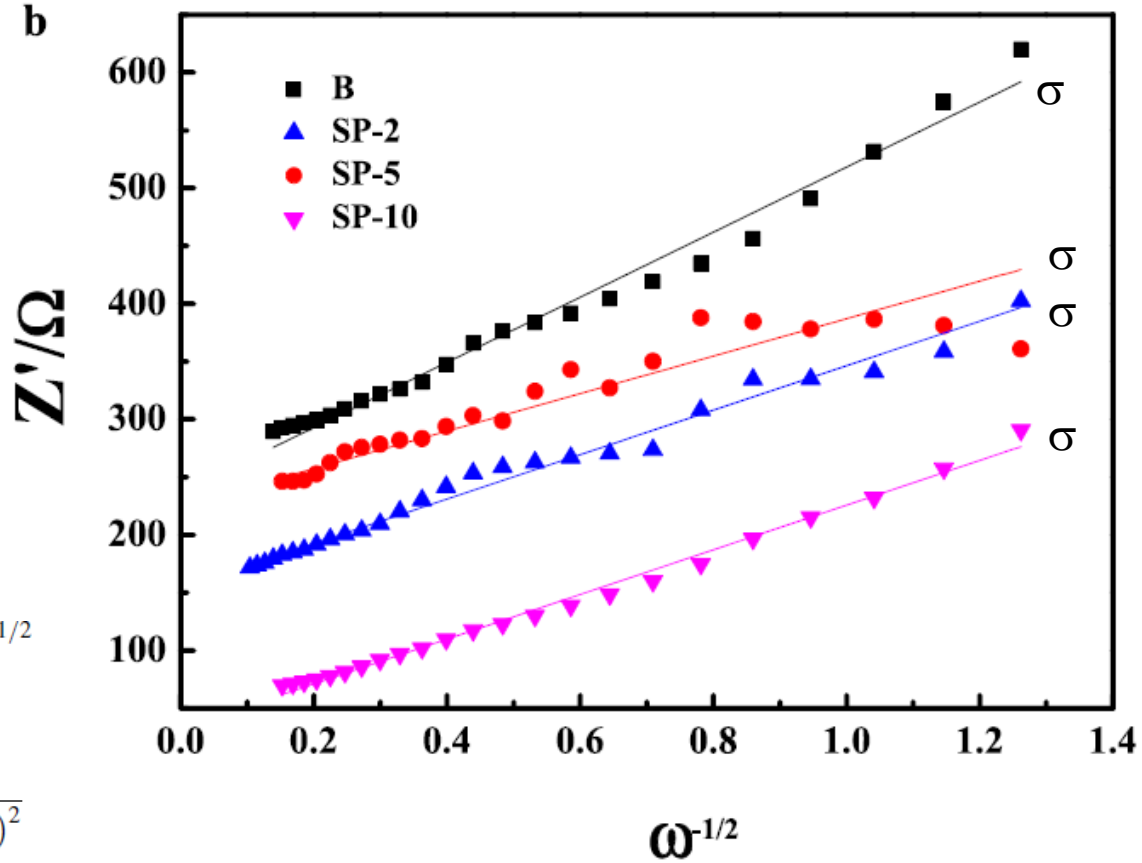
$$Z' = Zre = Rs + Rct + \sigma\omega^{-1/2}$$



Results – Nyquist plots

The D_{Li+} is:

- Al foil = 1.19×10^{-14} cm^2s^{-1}
- SP-2/Al = 2.63×10^{-14} cm^2s^{-1}
- SP-5/Al = 3.69×10^{-14} cm^2s^{-1}
- SP-10/Al = 2.60×10^{-14} cm^2s^{-1}



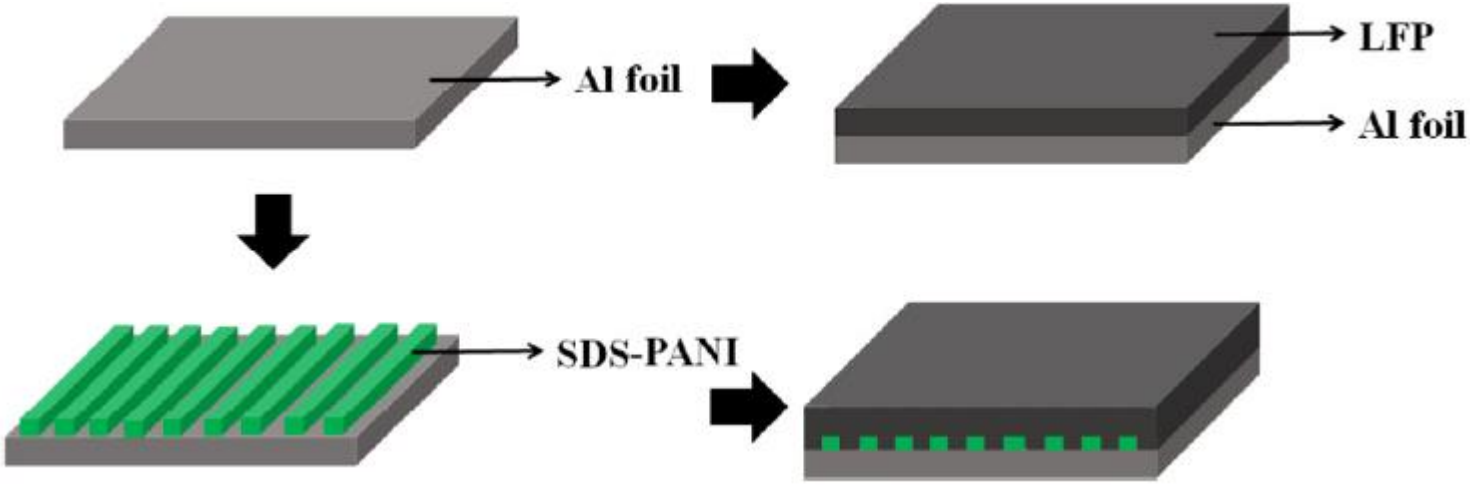
ω = 2πf. Rct

$$Z' = Zre = Rs + Rct + \sigma\omega^{-1/2}$$

Diffussion coefficient

$$D_{Li^+} = \frac{(RT)^2}{2(An^2F^2C_{Li^+}\sigma)^2}$$

Difference between the electrodes



Conclusion

- For the first time, a SDS-doped PANI film with a well-defined leaf stalk-shaped morphology was prepared onto the surface of the commercial Al foil using a CV method, producing a novel kind of current collector.
- The as-prepared films were thoroughly characterized by using SEM, FTIR and XRD, revealing that particles with a leaf stalk-shaped morphology were successfully fabricated in the presence of SDS and the main component of all as-prepared particles was PANI.
- Particularly, the average discharge capacity of LFP electrode assembled on the current collector of SP-5/Al at 5 C was nearly 30% higher than that of LFP prepared using the traditional current collector of pure Al, revealing that the rate capability of LFP could be remarkably enhanced through using the newly prepared SDS-doped film coated Al foil as the current collector.
- The greatly reduced charge transfer resistance, the larger lithium ion diffusion coefficient and the special leaf stalk-shaped morphology of the SDS-doped PANI particles were analyzed to be the main reasons endowing the current collector of SP-5/Al an evident promotion effect towards the electrochemical performance of a LFP electrode.

Thank you