Effect of Anionic, Cationic, and Non-ionic surfactants with NaF on the Performance of Soluble Lead Redox Flow Battery

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Soluble Lead Redox Flow Battery

Soluble Lead Redox Flow Battery (SLRFB)

Anode : $Pb^{+2}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$ $E^0_{-ve} = -0.13$ V vs. SHE

Cathode : $Pb^{+2}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$ $E^0_{+ve} = +1.49$ V vs. SHE

Cell Reaction : $2Pb^{+2}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons PbO_{2\,(s)} + Pb_{(s)} + 4H^+_{(aq)}$ $E^0_{cell} = 1.62$ V

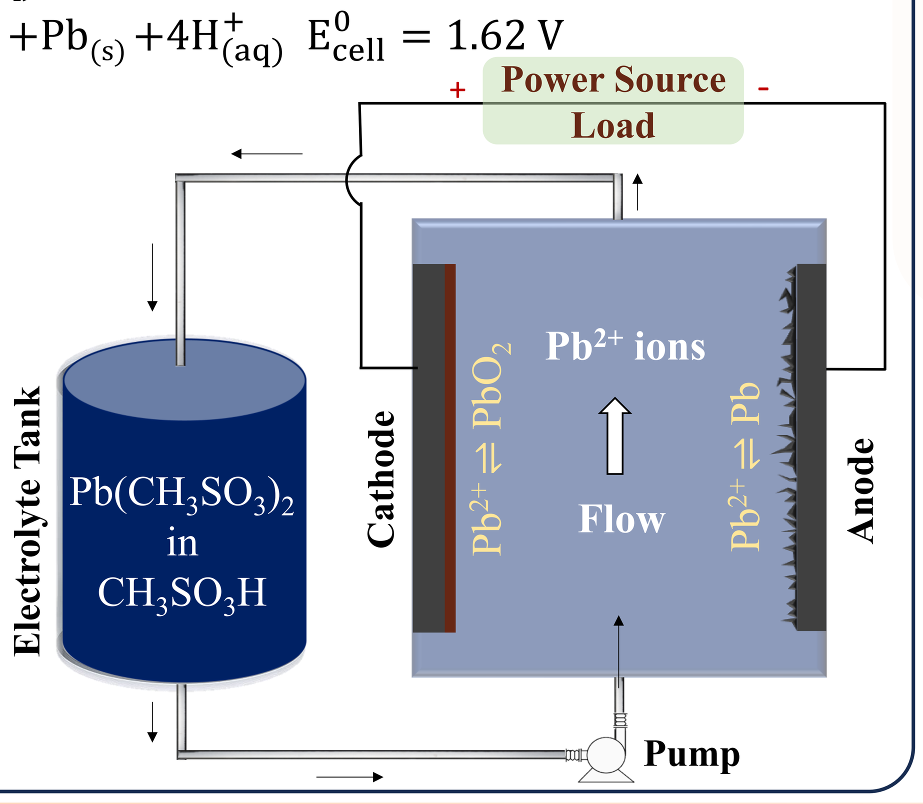
Advantages

Cost effective flow battery

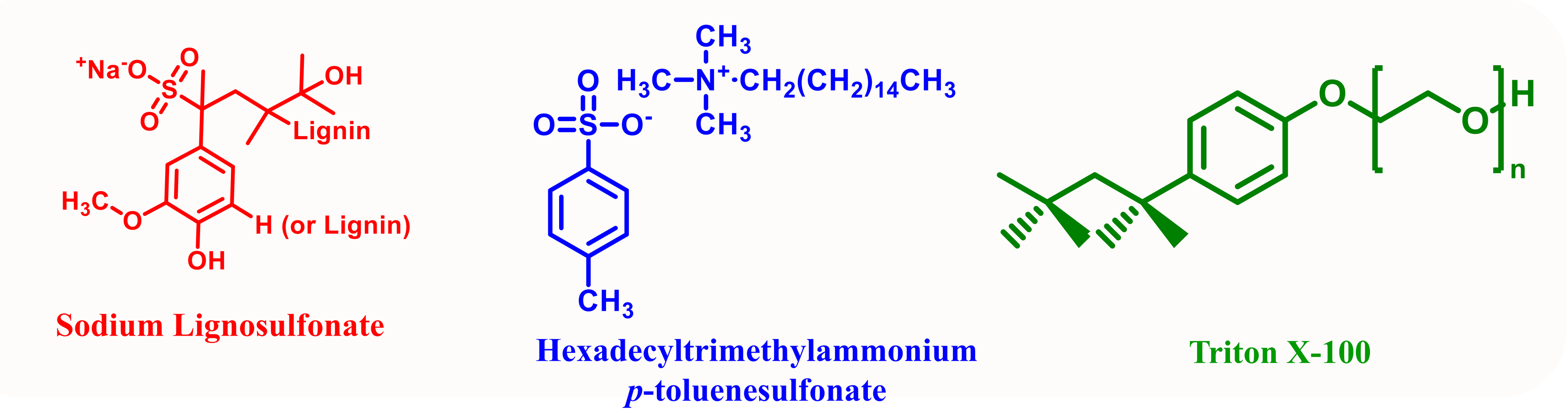
- Single electrolyte
- No cost-intensive ion-exchange membrane
- Widely abundant low-cost active materials

Challenges

- Pb dendrite formation on anode
- O_2 evolution reaction on cathode
- PbO_2 sludge formation
- Sluggish electrode kinetics of cathode



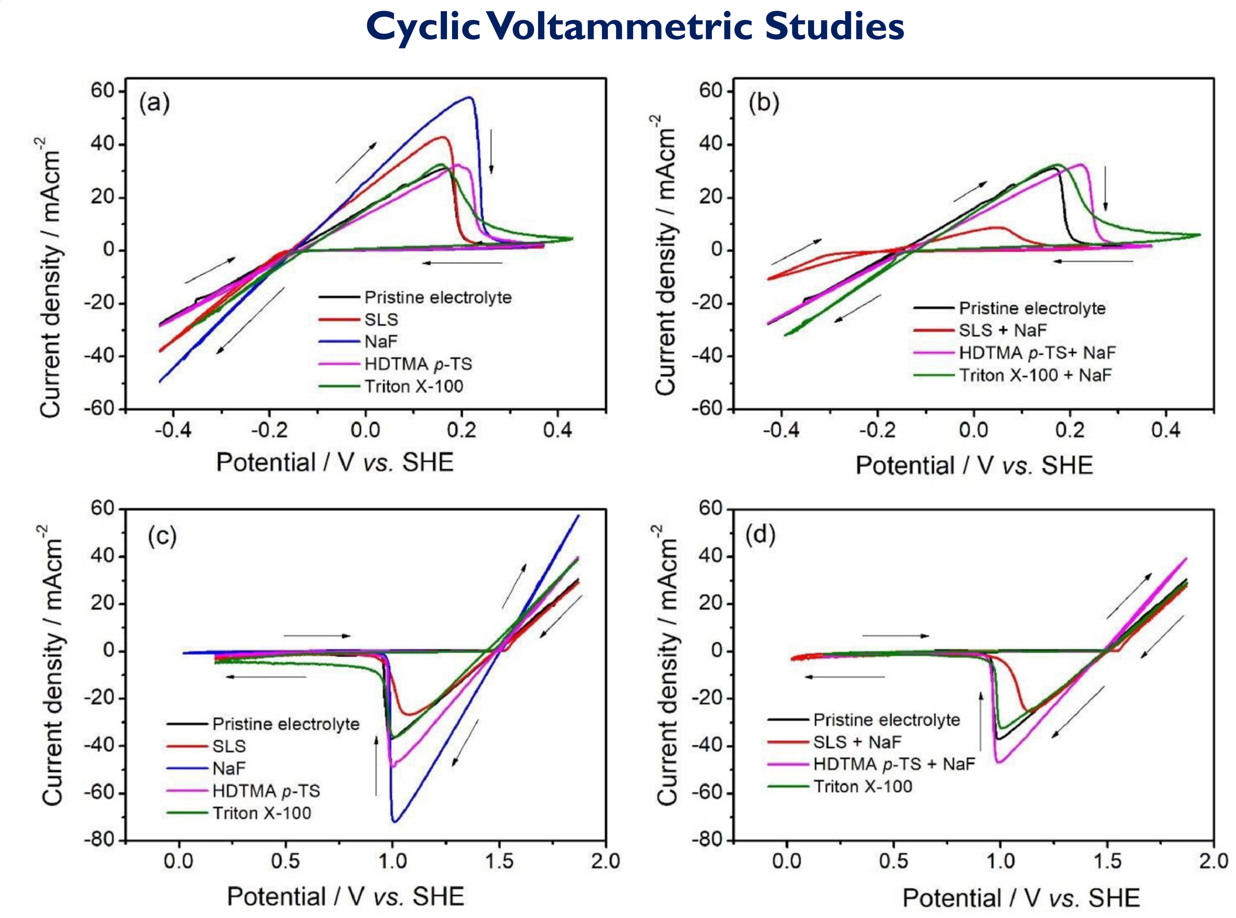
Role of Surfactants



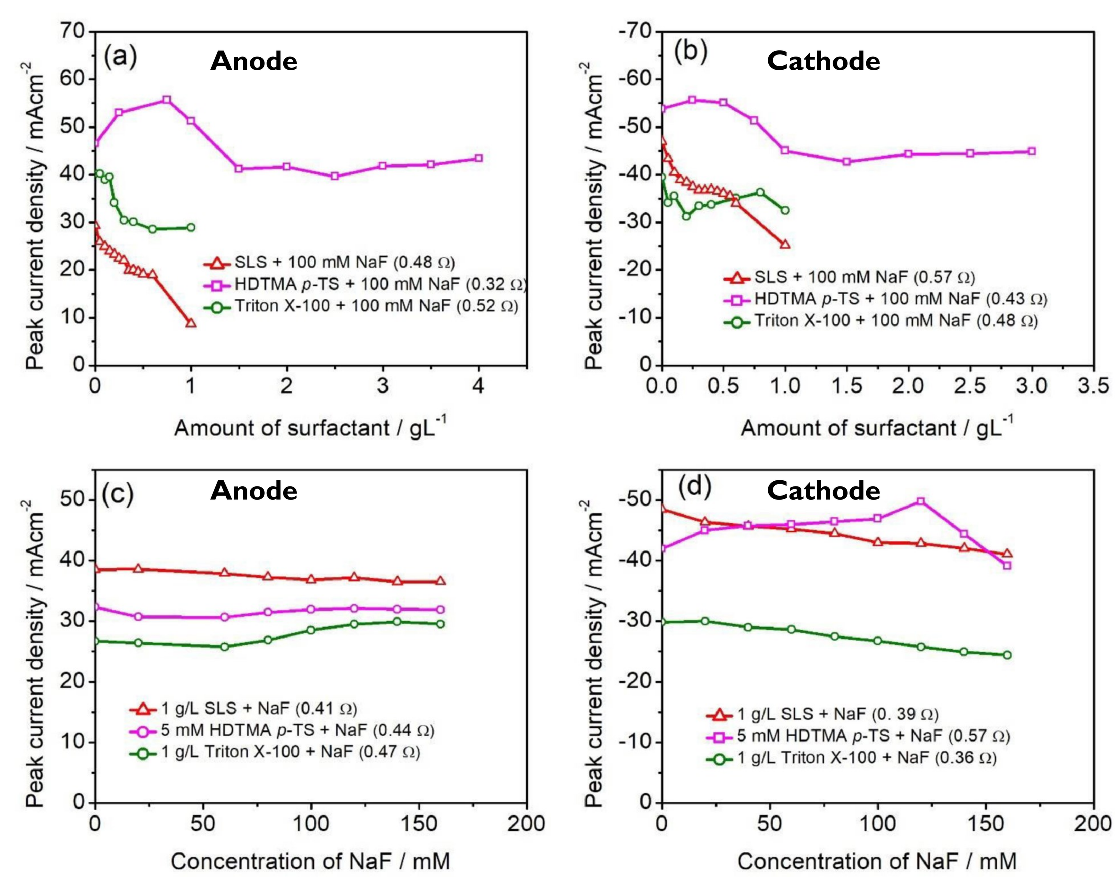
- Surfactants are compounds with a distinct structural arrangement of atoms forming hydrophobic and hydrophilic parts.
- The surfactant molecules in electrolytes agglomerate and form micelles of different shapes at above certain critical concentrations. The surfactant molecules or micelles adsorb onto the electrodes and may act as a physical barrier for the movement of ions and influence the electrochemical parameters such as diffusion coefficient of ions, ionic conductivity, and rate constant, etc.
- Depending on the direction of applied electric field and the applied voltage or current, the surfactant molecules or micelles tend to reorient themselves and migrate towards oppositely charged electrode and get adsorbed at the electrode-electrolyte interface
- Selecting a suitable polar surfactant as an additive could give preferential advantage to a specific electrode reaction.

Voltammetric Studies

Cyclic Voltammetric Studies

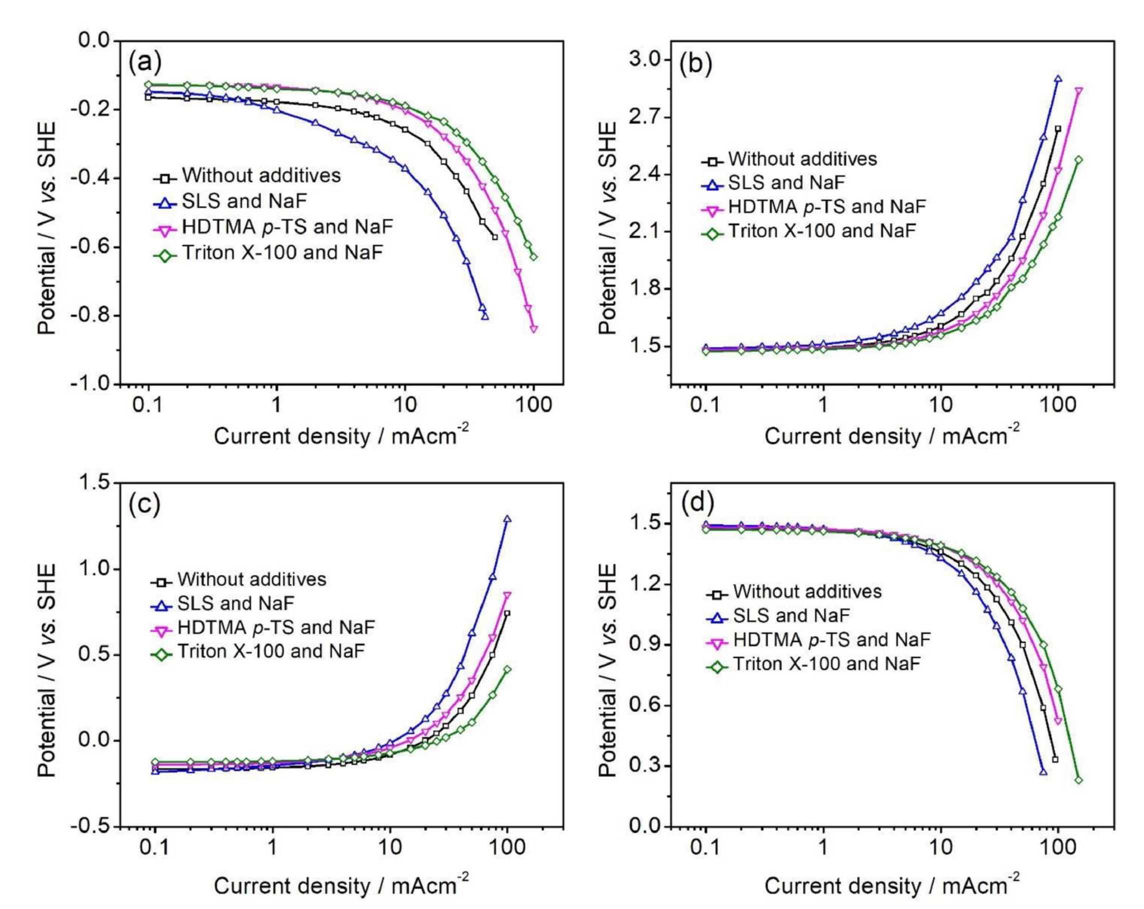


Effect of concentration of Surfactants and NaF



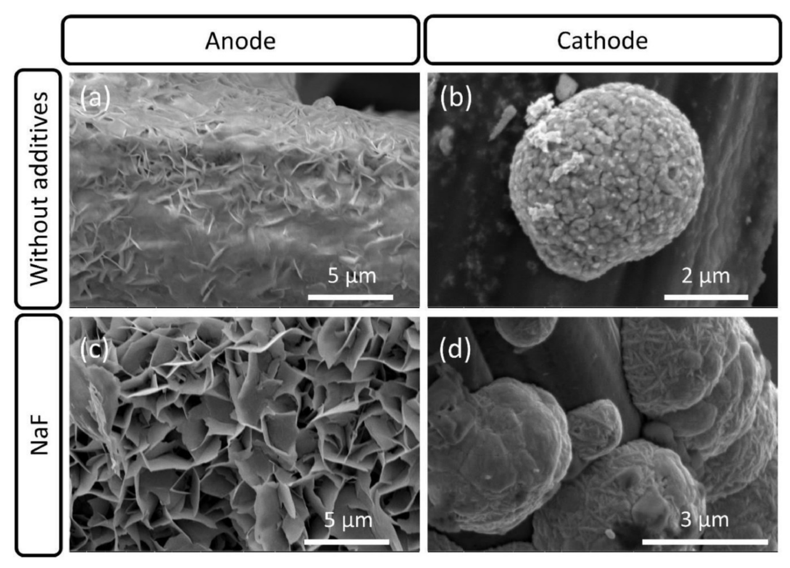
- The addition of a single additive to the electrolyte results in an increase in peak current density for both the anode and cathode compared to the pristine electrolyte, except when the electrolyte contains the SLS additive.
- Based on cyclic voltammetry studies, the binary additive combination of HDTMA *p*-TS and NaF is preferred over other binary additive combinations.
- Increasing surfactant concentration in an electrolyte with 100 mM NaF decreases peak current densities for the anode and cathode with SLS and Triton X-100. However, with HDTMA *p*-TS, the peak current density initially rises then steadies.
- The addition of NaF to the electrolyte with surfactants minimally impacts peak current densities, indicating surfactants on the electrode surface remain unaffected.

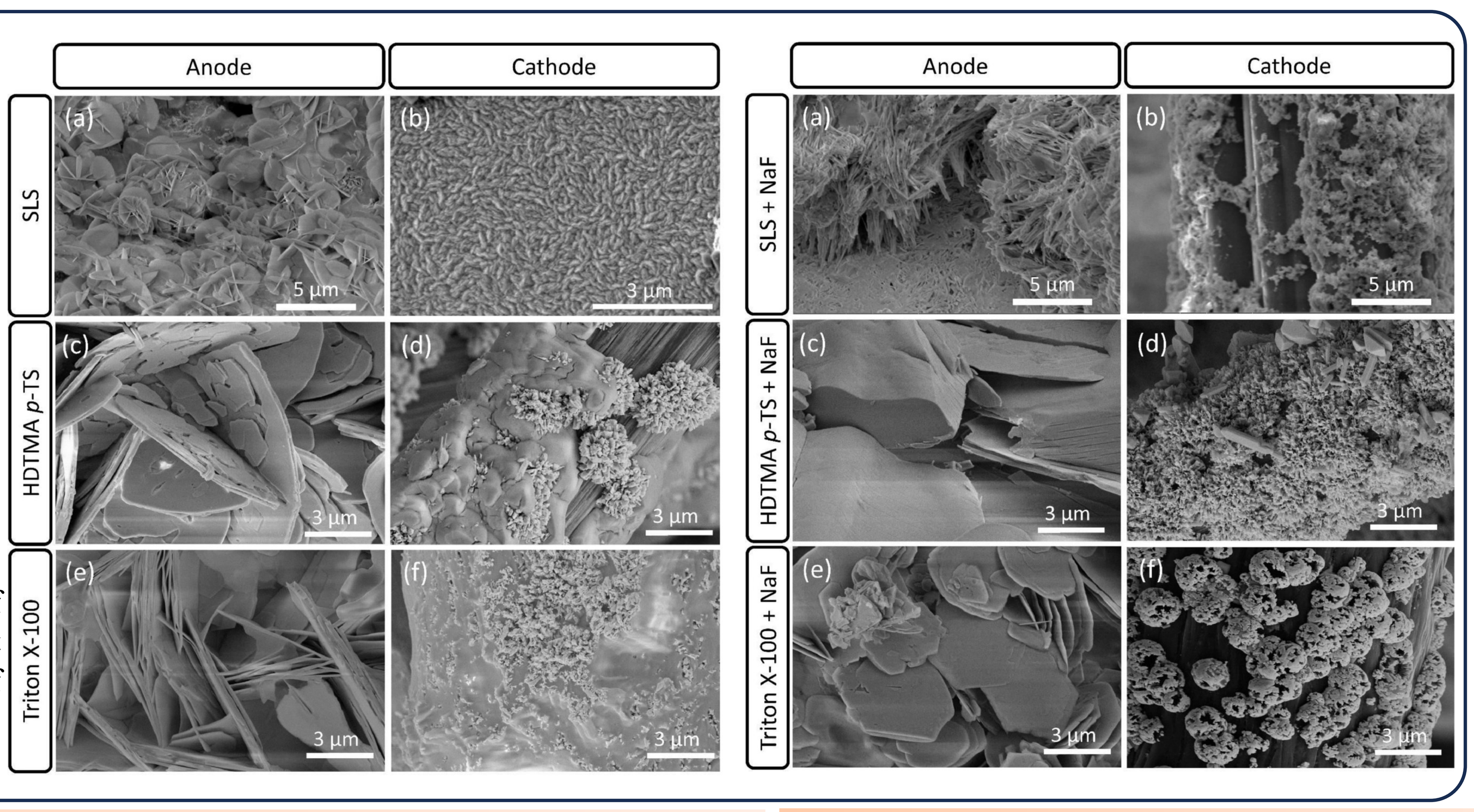
Electrode Polarisation Studies



- Overpotential for Pb and PbO_2 deposition and dissolution is highest with SLS and NaF binary additive system as compared to the pristine electrolyte, and electrolyte with other binary additive systems, making it polarise much faster than all other additive systems.

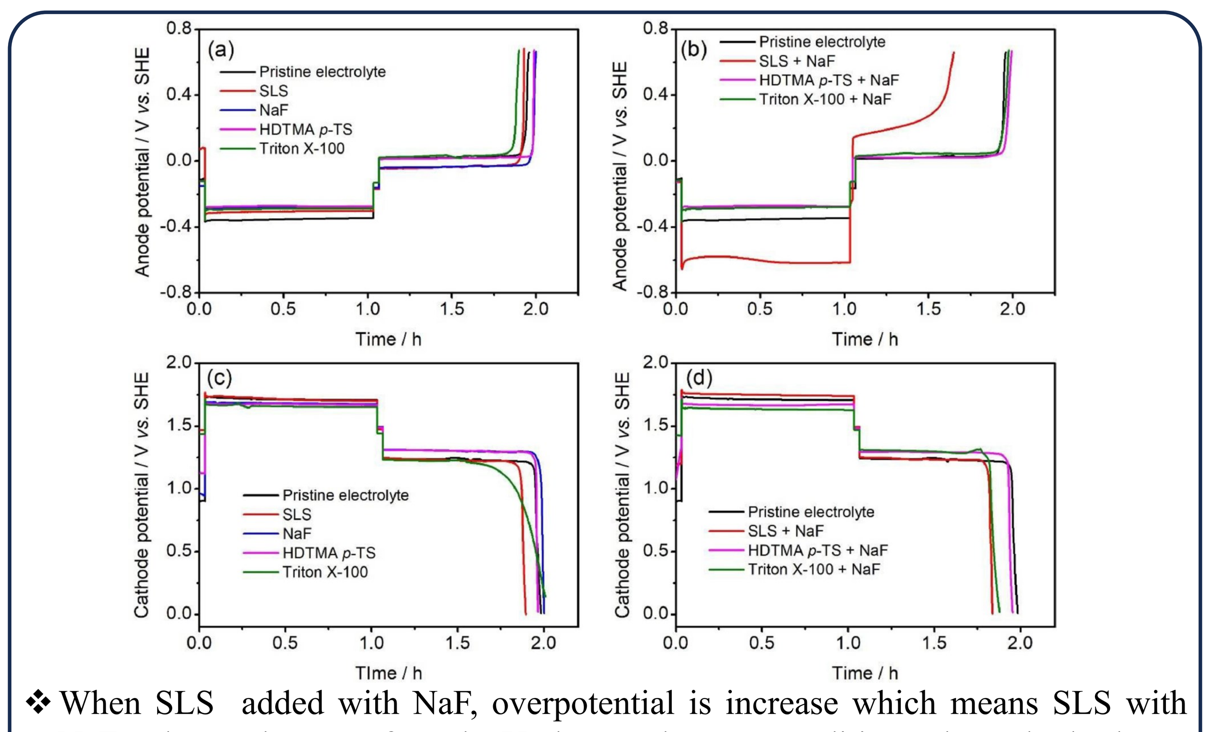
Morphological Studies





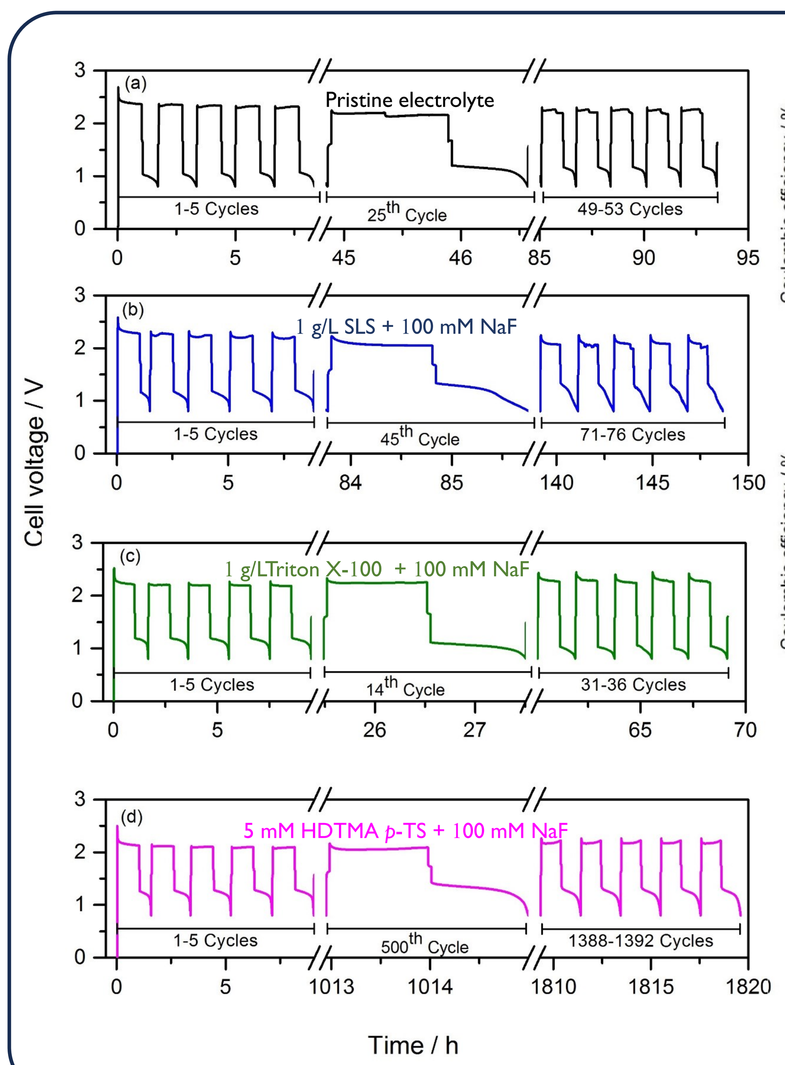
- HDTMA *p*-Ts+NaF system shows uniform deposit of Pb at anode compared to other additive system, and at cathode also there is uniform and porous deposition of PbO_2.
- FESEM images after 1h charge duration at 20 mAcm⁻².

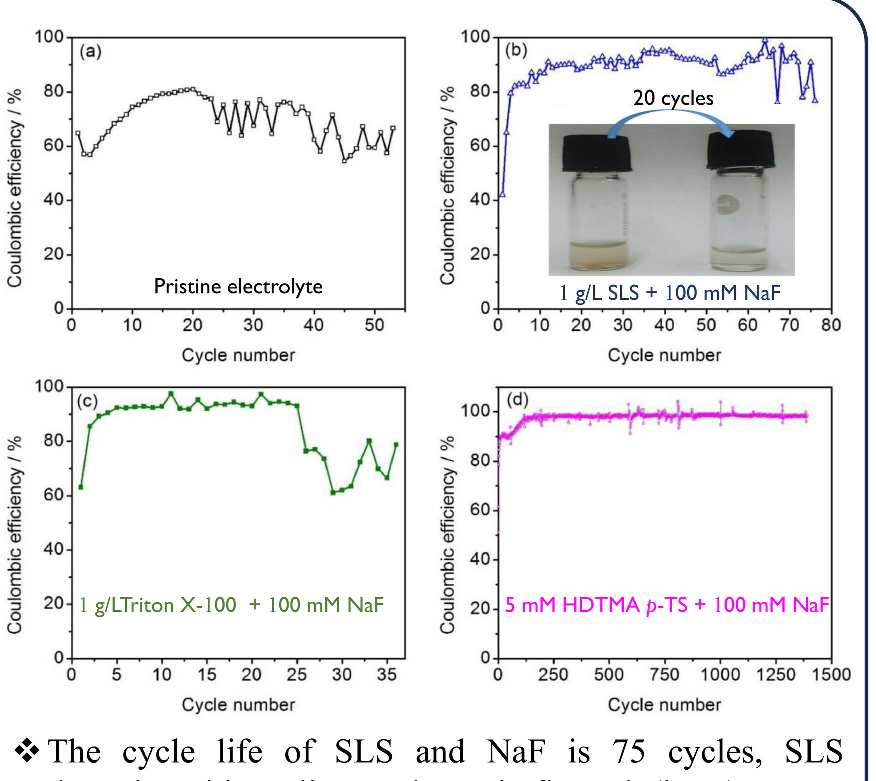
Galvanostatic Charge-discharge Studies



- When SLS added with NaF, overpotential is increase which means SLS with NaF reduces the rate of anode. Under steady-state conditions, the cathode shows a higher overpotential with SLS and NaF than with other electrolytes, but the lowest overpotential occurs with the Triton X-100 and NaF binary systems.

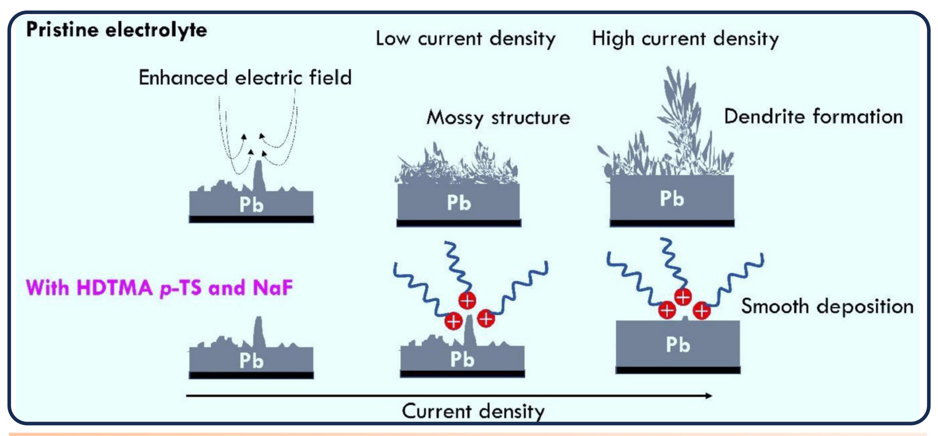
Life-cycle Studies





- The cycle life of SLS and NaF is 75 cycles, SLS degrades with cycling as shown in figure b (inset).
- Titan X-100 is not stable during cycling, resulting 25 cycles with NaF.
- HDTMA *p*-TS and NaF binary additive system helps in controlling the Pb dendrite formation, O_2 evolution and PbO_2 sludge formation and results in cycling stability of 1392 cycles without failure.

Mechanistic Insights



Acknowledgements

- Ministry of Education , India for providing Prime Minister Research Fellowship.
- UKRI – GCRF project SUNRISE (EP/P032591/1) and DST/TMD/MECSP/2K17/20 for providing the fund to the Project.

Conclusions

- FESEM studies reveal that HDTMA *p*-Ts and NaF binary additive system results in uniform deposition of Pb compared with other additive system.
- FESEM studies reveal that addition of NaF along with surfactant benefits cathode by facilitating the strong adhesion of PbO_2 resulting porous morphology.
- HDTMA *p*-TS and NaF binary additive system provide highest peak current density value among all the three binary additive system.
- Current polarisation studies of anode and cathode suggest that electrolyte with SLS and NaF binary additive suffer highest polarisation loss.
- HDTMA *p*-TS and NaF binary additive system helps in controlling the Pb dendrite formation, O_2 evolution and PbO_2 sludge formation and results in cycling stability of 1392 cycles without failure.
- The cycle life of SLS and NaF is 75 cycles, the concentration of SLS decreases with cycling and Titan X-100 is not stable during cycling, resulting 25 cycles with NaF.

References

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