Third Annual International Science and Technology Conference "Battery Innovation-2021"

Togliatty, March 18, 2021.

18 March 2021 Battery Innovation-2021 , Togliatty, Russia

Design principles of Pb-C additives for Lead-Carbon Battery

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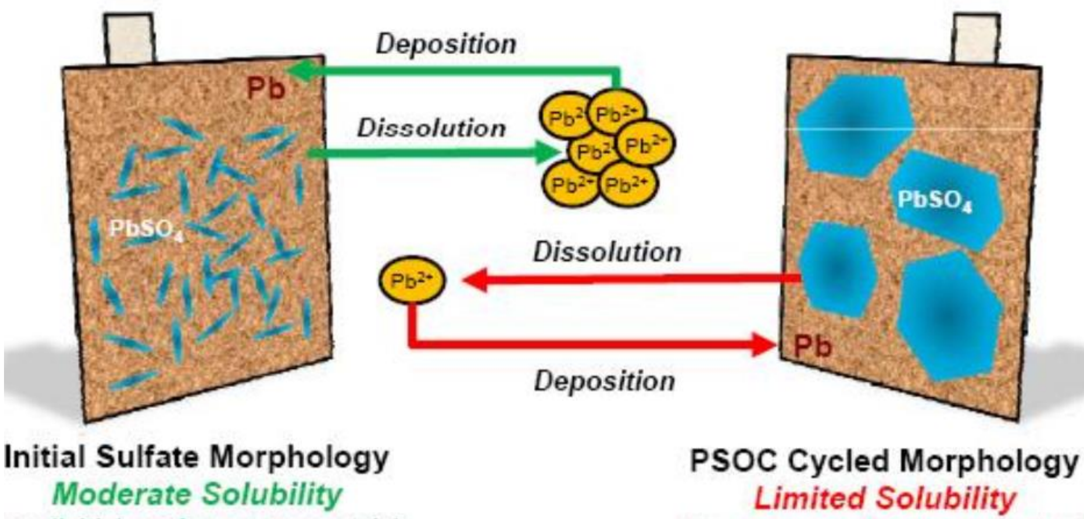
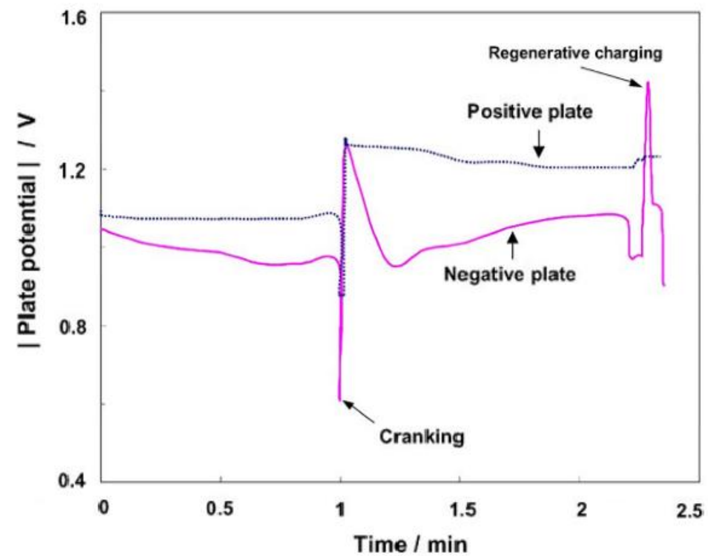
Sulfation of Pb electrode

Ostwald Ripening



Result: polarization of Pb electrode

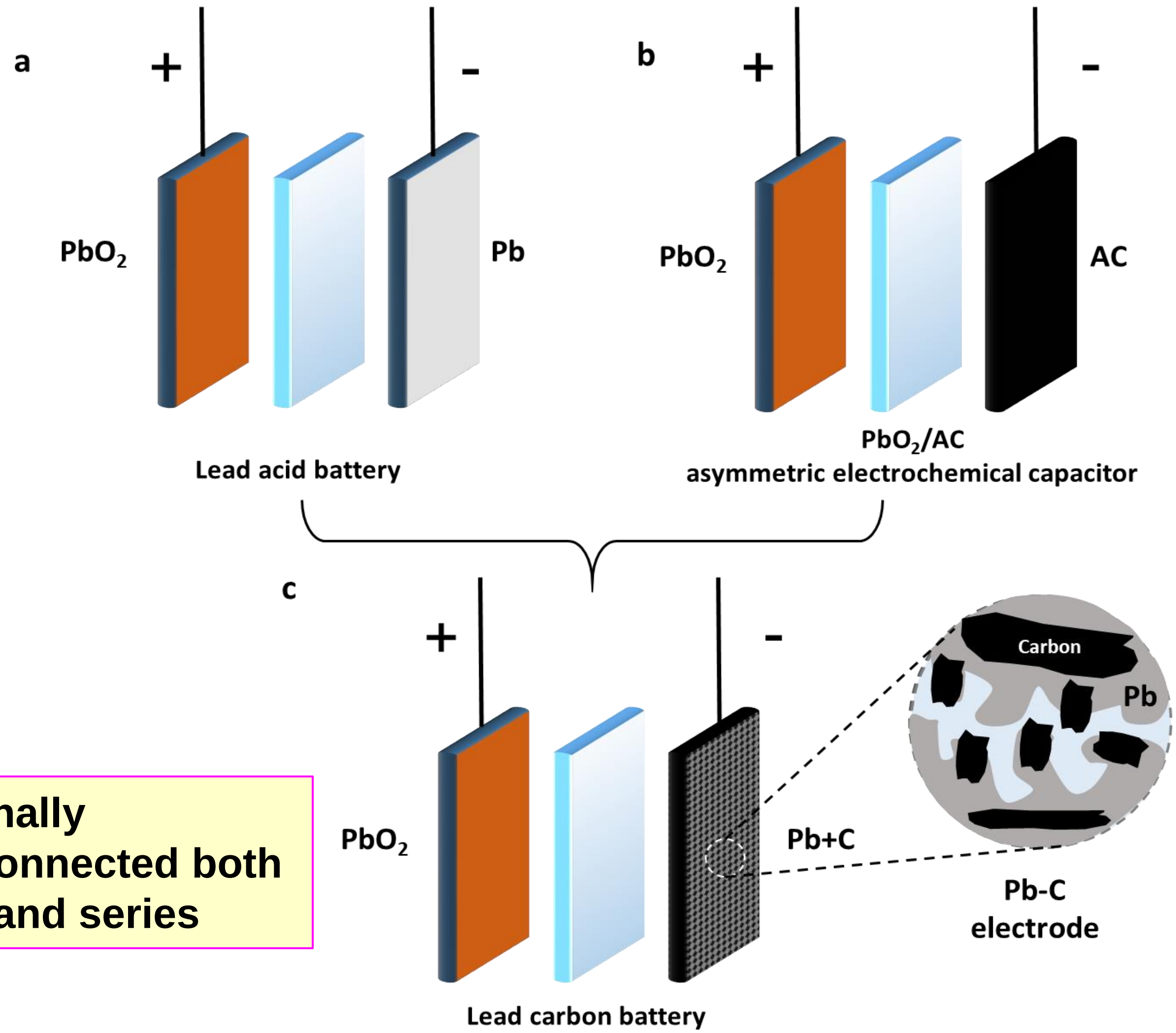


Sulfation of Pb electrode

- PSoC condition, Pb discharged to $PbSO_4$
- Small $PbSO_4$ particles grow up via Ostwald Ripening process
- High polarization, the chargeability of $PbSO_4$ decreased

L.T. Lam et al., ***Journal of Power Sources*** 133 (2004) 126–134

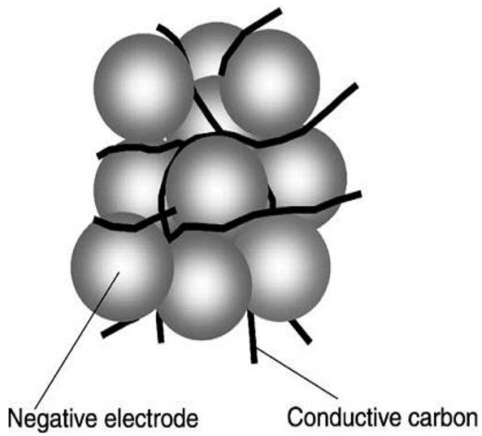
Lead Carbon Battery

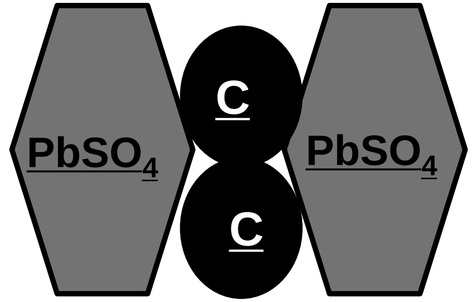


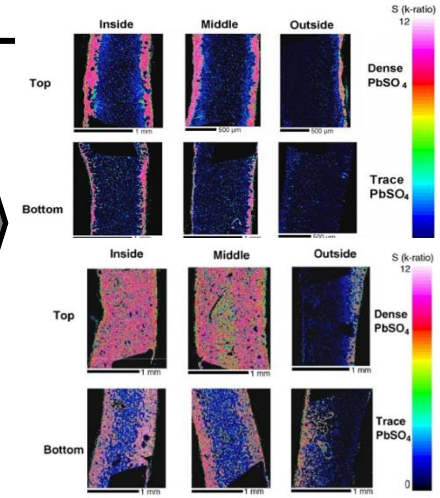
Internally
Pb and C are connected both in parallel and series

W.L. Zhang*, H. B. Lin*, X. Q. Qiu*, et al. Lead Carbon Batteries toward Future Energy Storage: from Mechanism, Materials to Applications, Submitted.

Mechanism of Carbon Materials

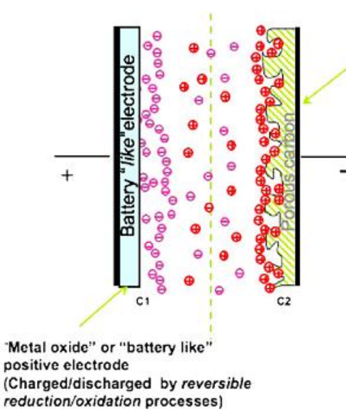


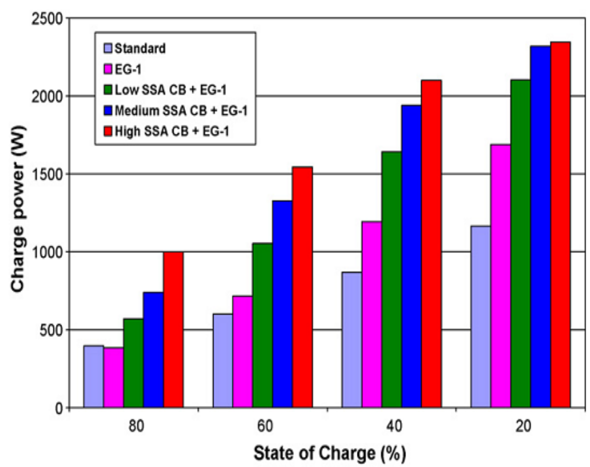


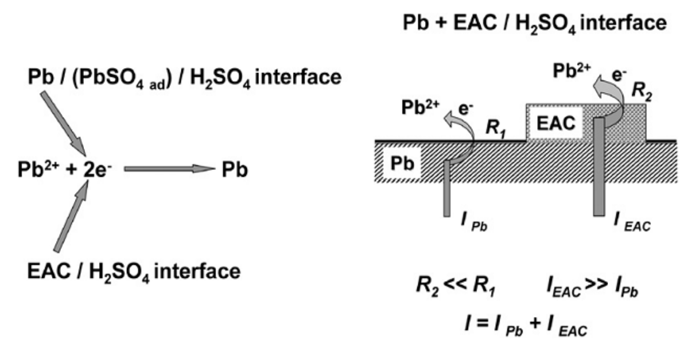


increase conductivity

steric hindrance





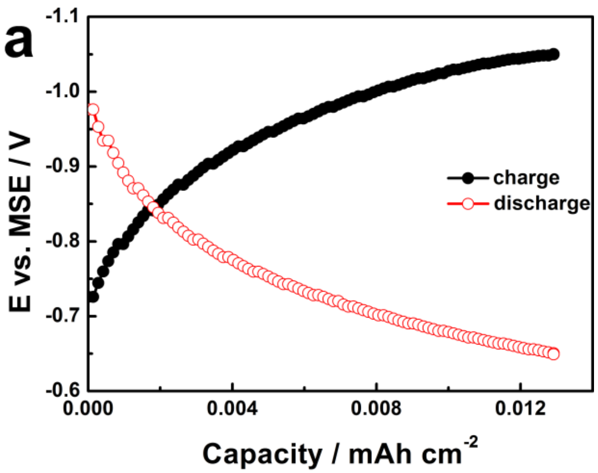


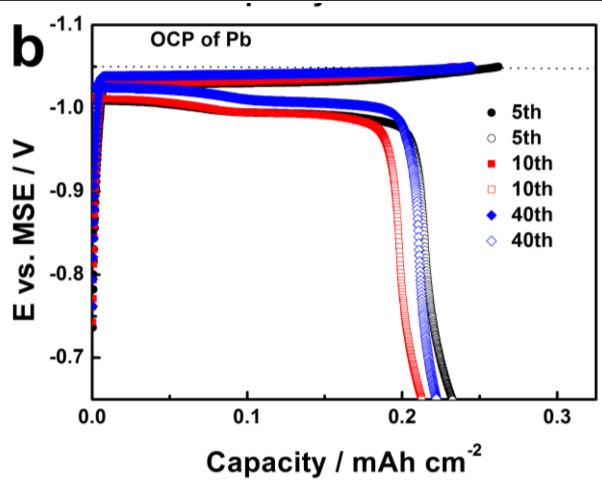
capacitive contribution

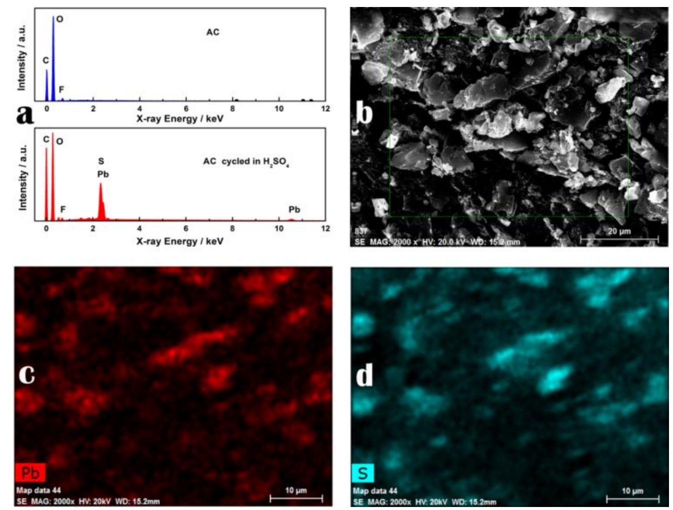
catalytic effect

[1] Shiomi, *et al*. ***Journal of Power Sources*** 64 (1997) 147-152; [2] J. Valenciano *et al.* ***Journal of Power Sources*** 158 (2006) 851–863; [3] M. Fernández, et. al., ***J. Power Sources***, 2010, 195: 4458–4469; [4] D. Pavlov et al. ***Journal of Power Sources*** 196 (2011) 5155–5167

Catalytic Deposition and 3D growth

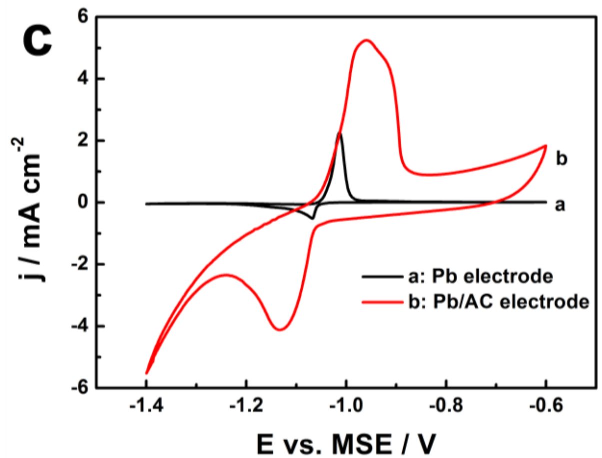






EDS spectra and mapping of Pb/AC electrode after 500 GCD cycles.

$$AC + PbSO_4 + H^+ + 2e^- \rightarrow AC \bullet Pb + HSO_4^-$$

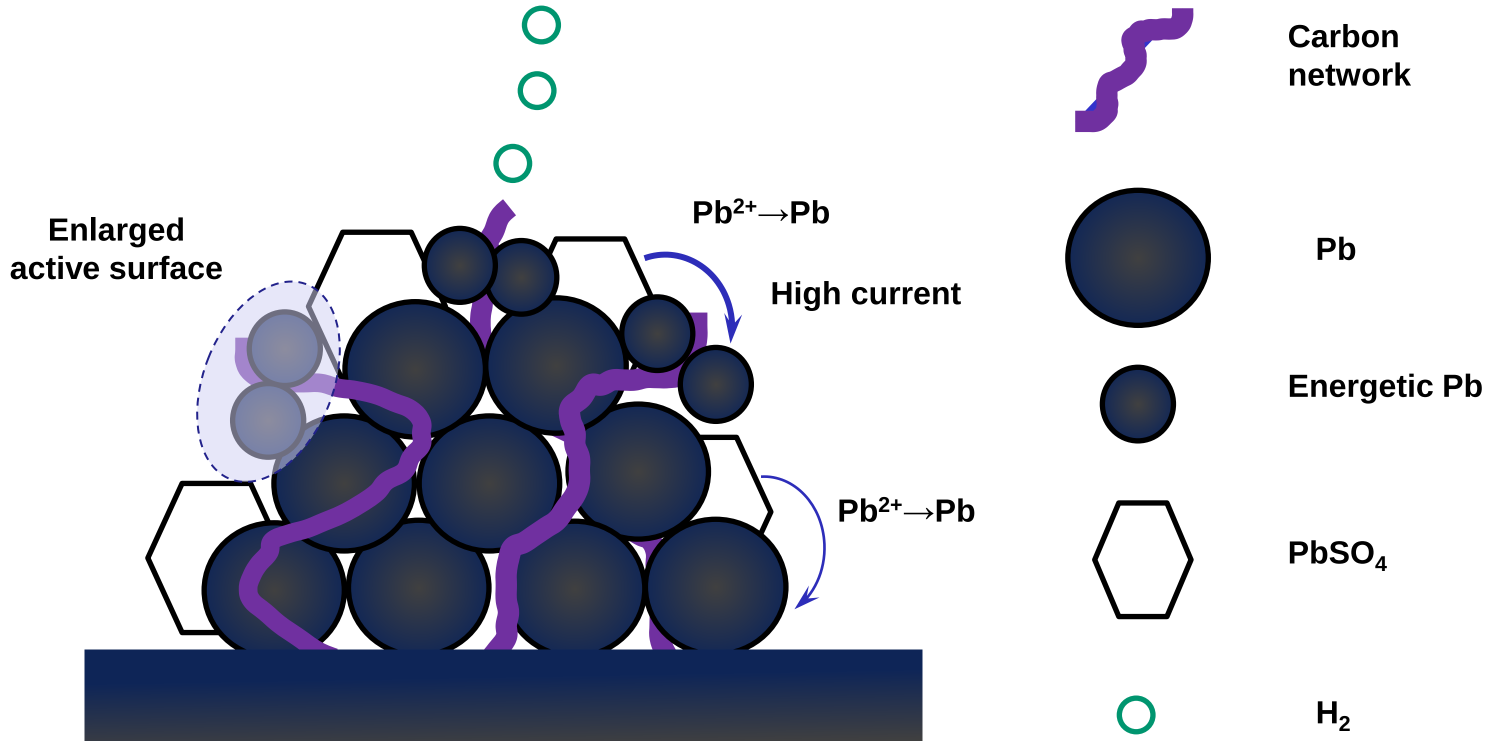


GCD of Pb/AC electrode in the potential range from -0.65 V to -1.05 V at 0.5 mA cm^{-2} (a)before and (b) after 500 GCD cycles, (c) CV curves.

Pb deposit on carbon provides a large portion of capacity
Catalytic deposition and 3D growth
Active sites on carbon: catalytic role, Pb seeds induce 3D growth

W.L. Zhang, H.B. Lin* et al., On the Electrochemical Origin of the Enhanced Charge Acceptance of the Lead-Carbon Electrode. ***J. Mater. Chem. A*** 2015, 3 (8), 4399–4404

Carbon Additives: Design Principles



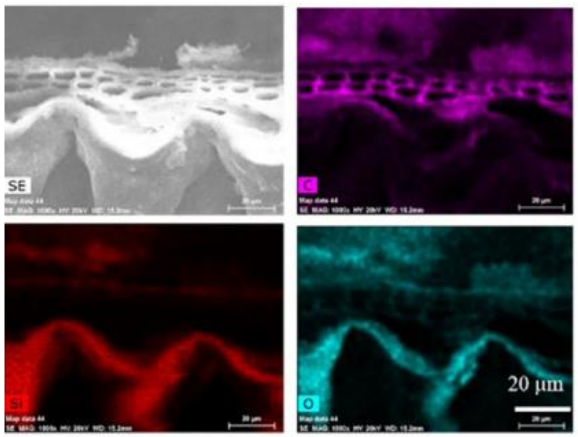
Requirements for Carbon:

Macroporous：for **the growth of 3D Pb** branches in **NAM**

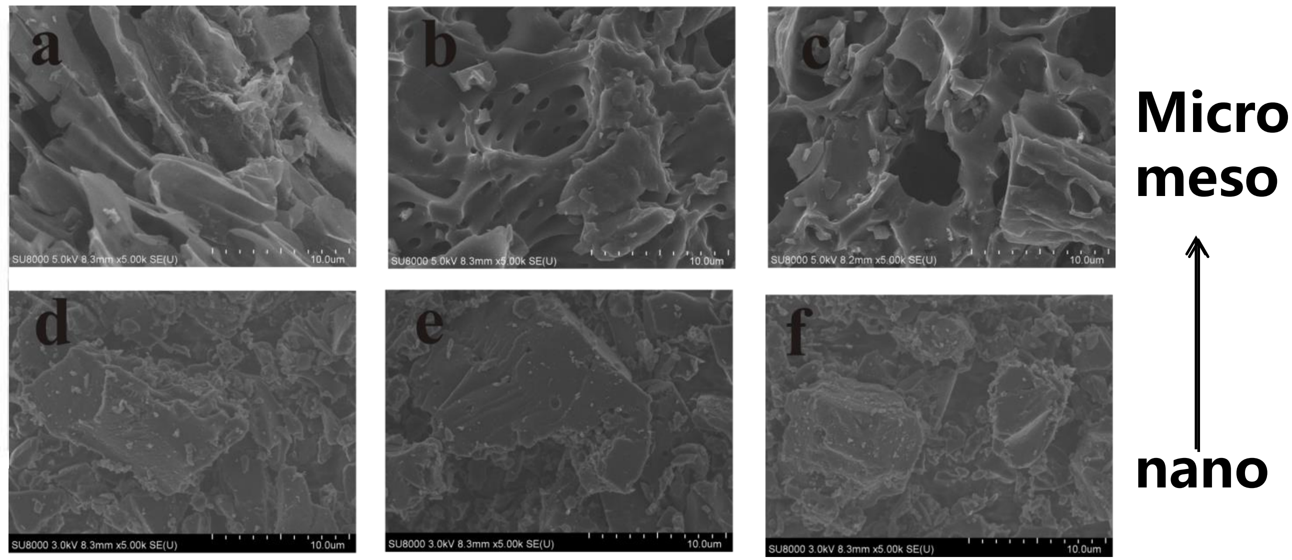
Affinity to Pb：**leadphilicity**： Pb seed induce the growth

Homogeneous distribution of **Pb seeds** or **active sites** for Pb growth, while parasitic HER is inhibited.

Structure of RHC



Elemental mapping of rice husk



SEM images of (a-c) RHC and (d-f) KAC.

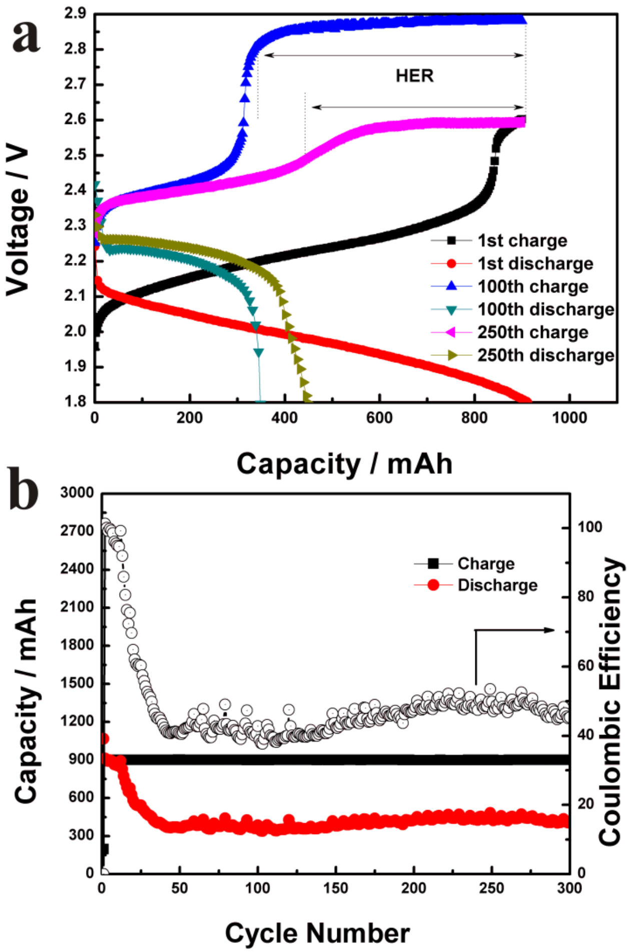
Table 6.3 Structural parameters of KAC and RHC

	Size/μm	Ash/%	S_{BET}/$m^2 \cdot g^{-1}$	V_{total}/$cm^3 \cdot g^{-1}$	V_{Micro}/$cm^3 \cdot g^{-1}$	V_{meso}/$cm^3 \cdot g^{-1}$
KAC	*Ca.* 5-8	0.3	1660	0.74	0.53	0.21
RHC	*Ca.* 40-50	~4.5%	247	0.191	0.0233	0.168

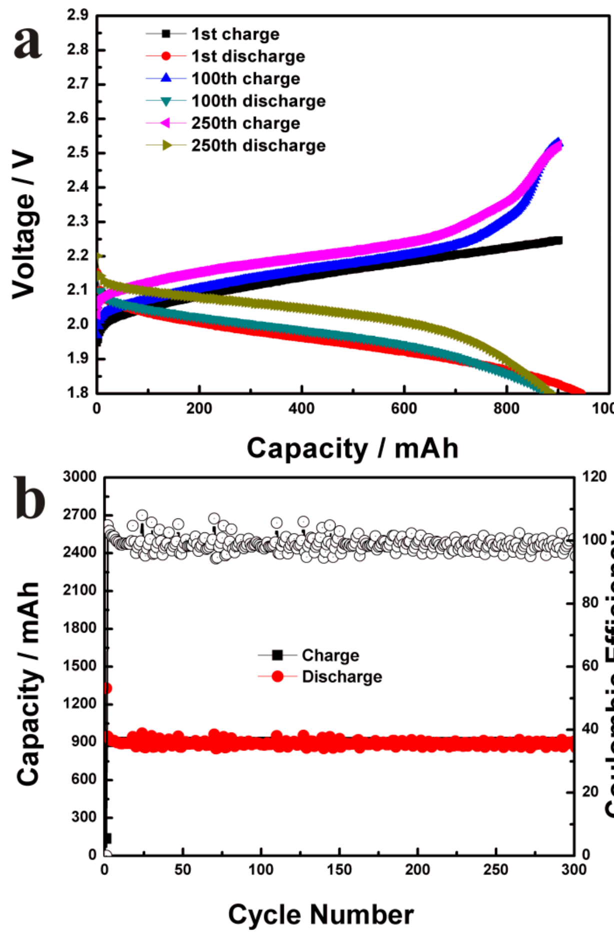
D.C. Liu. W.L. Zhang, W.M. Huang, ***Chinese Chem. Lett.*** 2019, 30 (6), 1315–1319.

W.L. Zhang, H.B. Lin*, et al. ***J. Power Sources*** 2017, 342, 183–191.

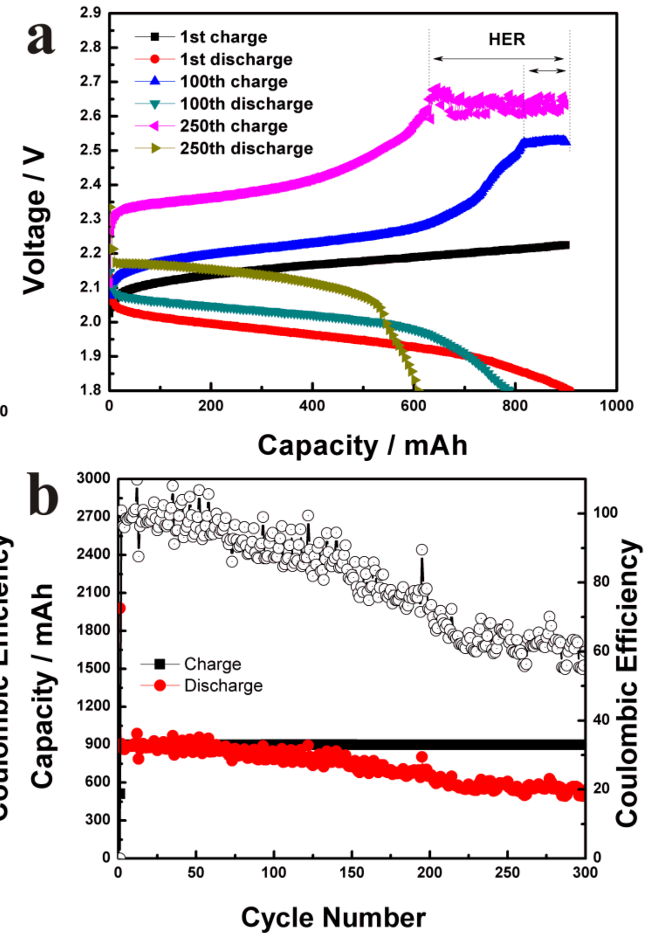
PSoC Performance



PSoC performance of **Control** electrode.



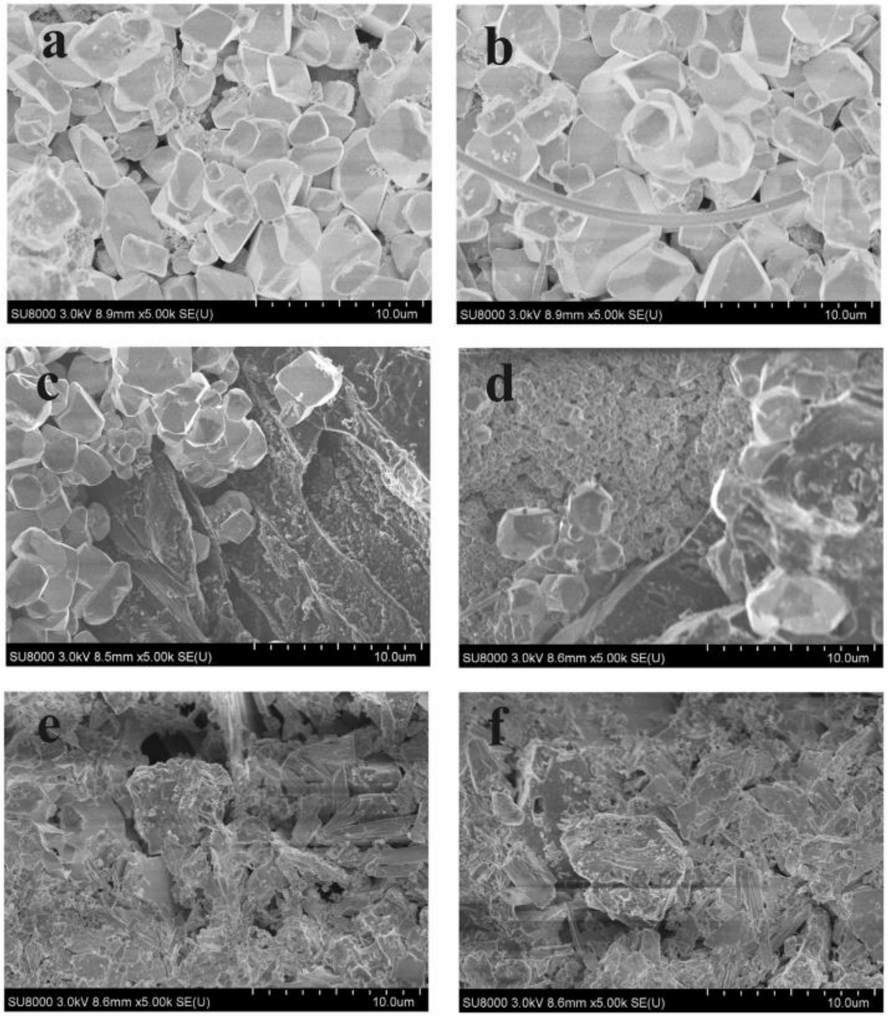
PSoC performance of **RHC** electrode.



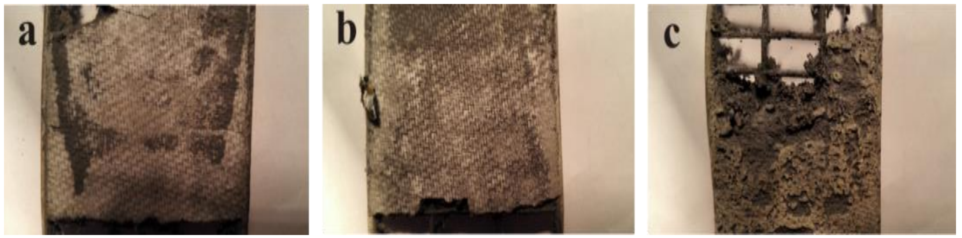
PSoC performance of **KAC** electrode.

W.L. Zhang, H.B. Lin*, et al. ***J. Power Sources*** 2017, 342, 183–191.

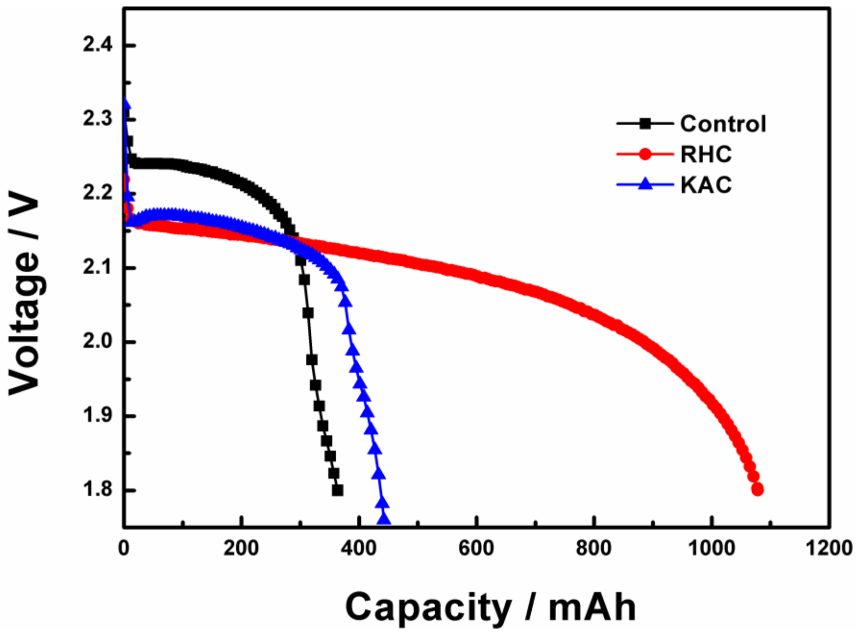
HRPSoC Performance



SEM images of （a, b） Control, **(c, d)** **RHC** and （e, f） KAC after PSoC.



Digital pictures of Control, **RHC** and KAC after PSoC test.

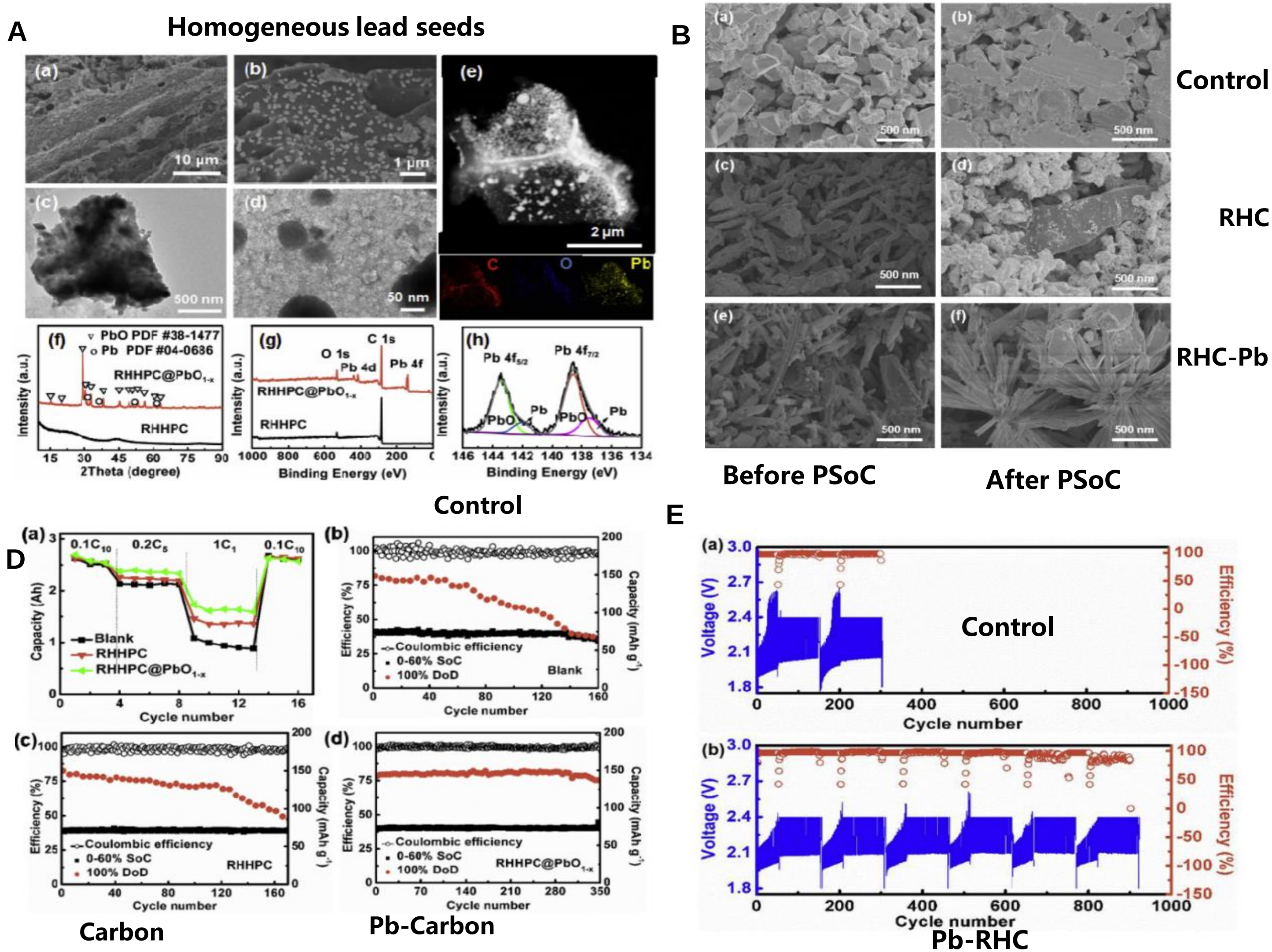


Discharge curve of Control， **RHC** and KAC after PSoC test.

W.L. Zhang, H.B. Lin*, et al**.** ***J. Power Sources*** 2017, 342, 183–191.

How to guide homogeneous deposition of Pb?

- **Homogeneous distribution of PbO seeds**,
- Continuous Pb-C structure, PbO reduction
- Good rate, and PSoC cycling,
- Under a standard IEC test mode, the PbRHC battery has a triple cycle life of conventional battery



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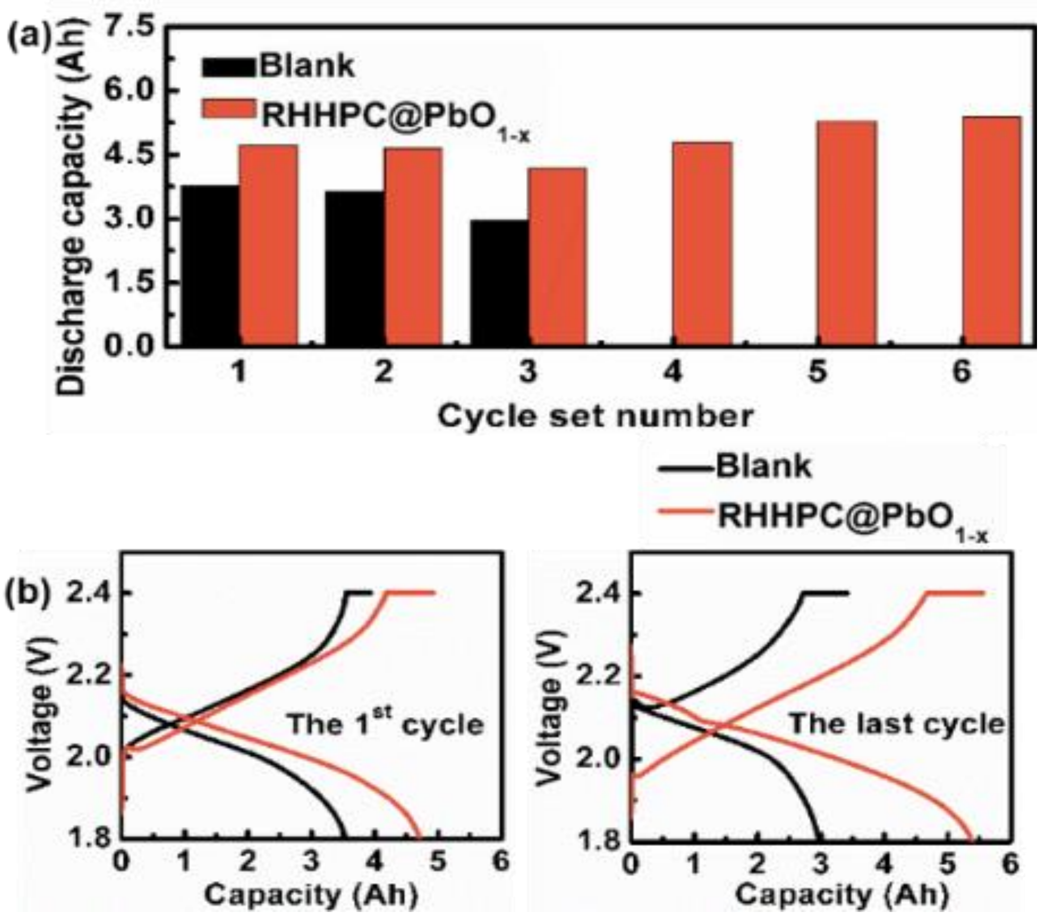
Details of PSoC Cycling



- Tested at a IEC 61427:2005 standard,
- Triple of the capacity of a conventional lead acid battery,
- After PSoC cycling, battery with RHHPC@PbO additive with increased capacity

(a) Discharge capacities for each cycle set and (b) the 1st and the last charge/discharge curves of the blank and RHHPC@PbO_{1-x} 2 V/4 Ah VRLA battery in the standard GB cycling test. The charge and discharge rates are $0.1C_{10}$. Reproduced with permission from Ref. [12] Copyright 2020, Elsevier.

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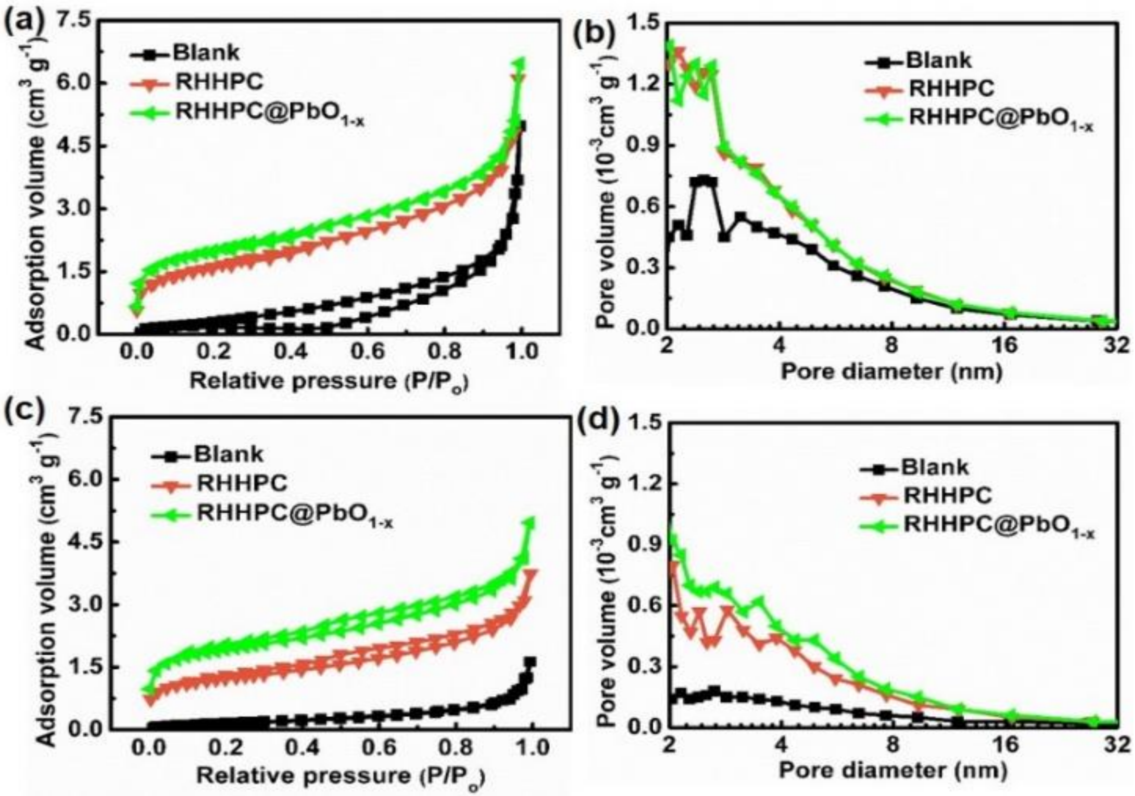
Influence of PSoC Cycling on Pore Architecture



(a) N_2 adsorption/desorption isotherms and (b) pore size distributions of the lead-carbon electrodes before PSoC tests; (c) N_2 adsorption/desorption isotherms and (d) pore size distributions of the lead-carbon electrodes after PSoC operation.

Lead-carbon electrode	Before PSoC operation			After PSoC operation		
	S_{BET} ($m^2 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)	V_{total} ($cm^3 \cdot g^{-1}$)	S_{BET} ($m^2 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)	V_{total} ($cm^3 \cdot g^{-1}$)
Blank	1.46	0.008	0.008	0.51	0.003	0.003
RHHPC	5.70	0.007	0.009	4.07	0.004	0.006
RHHPC@PbO_{1-x}	6.81	0.007	0.010	6.50	0.005	0.008

- Negative plates with additive, pore size and pore volume maintained,
- BET surface area only decreased by 4.5%, RHHPC@PbO_{1-x} additive is effective provide 3D growth Pb
- Significance of SSA, and high affinity between **Pb** and **C**

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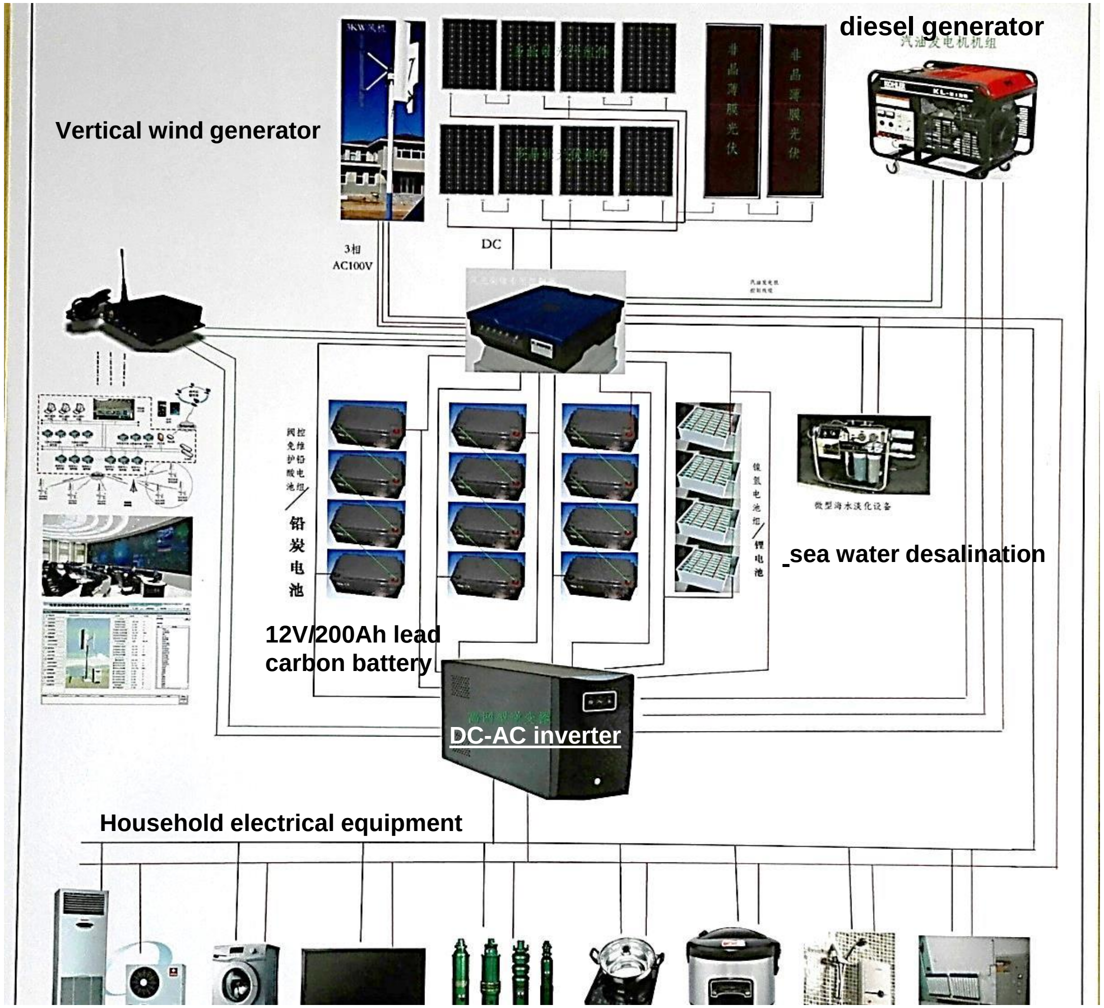
Utility Applications: Demonstration in Off-Grid Energy Storage

Inner Mongolia 8kW wind and photovoltaic hybrid power off-grid lead carbon energy storage system



SUMMARY：Where are We Heading to?

Opportunities and considerations:

Long cycle life under PSoC operation,
stability of negative plates could be achieved.

- **Defects:** Surface functional groups, edge defects active for Pb growth,
- **Specific surface area:** optimized for Pb growth (macrospores and large mesopores)
- **Trade-off**: Simultaneous HER inhibition and Pb growth

Challenges & issues toward commercialization:

Connection of Pb and C, HER, paste mixing

- **Issue:** Affinity between Pb and C
- **Solution:** homogeneous distribution of Pb on C for effective 3D growth of Pb.
- **Issue:** HER (practical battery)
- **Solution:** Pb and C composite, high HER overpotential metals,
- **Issue:** Paste mixing (**Industry**)
- **Solution:** Pre-mixing with leady oxide to enhance the density.

Selective PUBLICATIONS

Negative Active Materials

1. W.L. Zhang*, H. B. Lin*, X. Q. Qiu*, et al. Lead Carbon Batteries toward Future Energy Storage: from Mechanism, Materials to Applications (Review), 2021, Submitted.
2. Z.Q. Lin, N. Lin, H.B. Lin*, W.L. Zhang*, ***Electrochim. Acta*** 2020, 338, 135868. (lead carbon negative electrode)
3. J. Yin, N. Lin, Z.Q. Lin, H.B. Lin*, W.L. Zhang*, ***Energy*** 2020, 193, 116675. (lead carbon negative electrode)
4. J. Yin, N. Lin, Z.Q. Lin, H.B. Lin*, W.L. Zhang*, ***J. Electroanal. Chem.*** 2019, 832, 152–157. (Electrolyte)
5. J Yin, N Lin, W Zhang, Z Lin, Z Zhang, Y Wang, J Shi, J Bao, H.B. Lin*, ***Journal of energy chemistry*** 2019, 27 (6), 1674-1683. (lead carbon negative electrode)
6. W.L. Zhang, H.B. Lin*, et al. ***J. Power Sources*** 2017, 342, 183–191. (lead carbon negative electrode)
7. W.L. Zhang, H.B. Lin* et al., On the Electrochemical Origin of the Enhanced Charge Acceptance of the Lead-Carbon Electrode. ***J. Mater. Chem. A*** 2015, 3 (8), 4399–4404. (Mechanism)

ACKNOWLEDGEMENTS

THANK YOU FOR YOUR ATTENTION!

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