

# Lead-Carbon Battery Negative Electrodes: Mechanism and Materials

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## Abstract

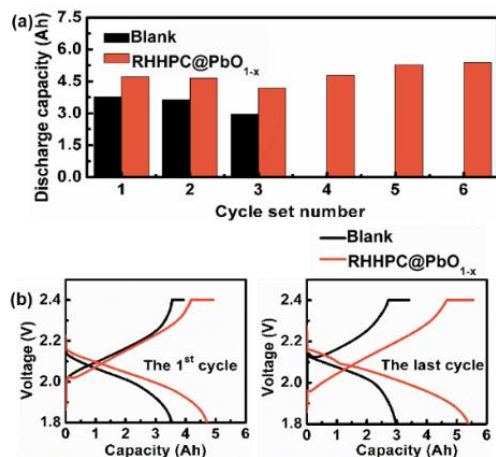
Lead-carbon batteries have become a game-changer in the large-scale storage of electricity generated from renewable energy. During the past five years, we have been working on the mechanism, additives and battery architecture design of lead-carbon batteries. We demonstrated the electrochemical origin of the enhanced charge acceptance of lead-carbon battery, and developed effective composite additives based on porous carbons for high-performance lead-carbon electrodes and lead-carbon batteries. Our lead-carbon batteries show high-performance under partial state of charge (PSoC) and high-rate PSoC duties. This paper gives audiences an overview of our work on lead-carbon batteries in the recent five years.

**Key words:** Lead-Carbon Electrode, Lead-Acid Battery, Carbon, Charge Acceptance, Partial State of Charge.

Lead-Acid Battery (LAB) dominates medium to large scale energy storages from applications of start, light and ignition (SLI) in automobile, telecommunication, uninterruptable power supply (UPS), remote area power supply to renewable energy storage. LAB is the most important rechargeable battery in our daily lives. In the 21<sup>st</sup> century, with the fast development of renewable energy storage and hybrid electric vehicles, various batteries have to be operated in the conditions of half fully charged. In these cases, LABs are required to work under partial state of charge (PSoC) duties, such as hybrid electric vehicles and the grid-scale energy storage of electricity generated from renewable energy. PSoC is an emerging battery operation duty that puts much higher standards on LAB compared with the traditional operational modes.[1] The charge acceptance of lead negative electrode needs to be improved due to the severe sulfation of negative electrode in LAB operated in PSoC duty. Sulfation is not a phenomenon only occurs in PSoC.[2] However, sulfation of the negative electrode becomes a severe problem when LAB is operated under PSoC for a long time.[3] Since new generated small PbSO<sub>4</sub> particles tend to grow to ultra-large particles that are hard to be recharged to their active state (sponge lead) under the Ostwald Ripening process. The sulfation problem can be partially resolved by the addition of carbonaceous materials in the negative active material (NAM) of LAB. Fortunately, LAB with functionalized carbon materials in its NAM shows superior performance when operated under PSoC duty. Due to their superior performances, nowadays, these advanced LABs are called lead-carbon battery (LCB).

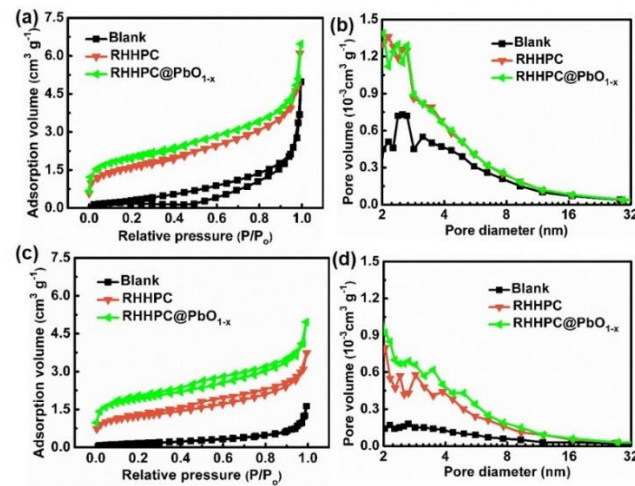
The function of carbonaceous materials in NAM of LCB can not be easily elaborated due to the complex physicochemical environments of lead-carbon electrodes (the recrystallization of insulating  $\text{PbSO}_4$ , conductive Pb skeleton and branches, and variation of microstructures during charge-discharge). Phenomenologically, many possible electrochemical origins of the enhanced charge acceptance of lead-carbon negative electrode in LCB have been proposed. The possible contributions of carbonaceous materials in lead-carbon electrodes are: increasing conductivity, enhancing the specific surface area (electrochemical active surface area) of energetic Pb, steric hindrance for separating the agglomeration of  $\text{PbSO}_4$  and Pb, and capacitive capacity contribution. We studied the electrochemical origin of the enhanced charge acceptance of lead-carbon electrode by various electrochemical methods, such as electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and chronoamperometry [4]. We found that the capacity contribution of a capacitive activated carbon is not significant due to the mismatching between the high working potential range of activated carbon (-0.9 V to 0.4 V vs. mercurous sulfate electrode, MSE) and the low working potential of Pb/ $\text{PbSO}_4$  (-1.05 V). Through the *in-situ* growth of energetic Pb on the carbon in a binary lead-carbon electrode system, the Faradaic reaction contributes more to the whole capacity of a binary lead-carbon electrode. We thus conclude that the electrochemically active surface area of energetic Pb plays the most important role in the electrochemical performance of a lead-carbon binary electrode system. Porous carbons provide an extra electrochemical active surface for the growth of energetic Pb branches, contributing to increased capacity and enhanced charge acceptance.

In this regard, how to enlarge the electrochemical active surface area becomes crucial in LCB system. We have revisited the literature published 30 years ago by *Prof. Detchko Pavlov (Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences)*. [5] The lead negative electrode in LAB is in micron-scale and is composed of Pb skeletons with energetic Pb branches on their top. We chose a kind of rice-husk based hierarchical porous carbon (RHHPC) that has similar micron-scale porous structures with the NAM of Pb negative electrode [1]. Using this RHHPC as negative electrode additive, the lead-carbon electrode shows much more superior performance compared with the lead negative electrode and the lead-carbon electrode with capacitive carbon additives under PSoC operation [1]. Lead energetic branches growing on the inner surfaces of macropores of RHC acts as energetic branches and contributes to the capacity of Pb electrode. RHHPC based lead-carbon electrode show superior performances in a partial state of charge operation from 60% SoC to 0 SoC [1].



**Fig. 1** (a) Discharge capacities for each cycle set and (b) the 1<sup>st</sup> and the last charge/discharge curves of the blank and RHHPC@PbO<sub>1-x</sub> 2 V/4 Ah VRLA battery in the standard GB cycling test. The charge and discharge rates are 0.1C<sub>10</sub>. [Reproduced with permission from Ref. \[12\] Copyright 2020, Elsevier.](#)

Unfortunately, carbon additives show low hydrogen evolution overpotentials compared with lead. Therefore, we aim to improve the low hydrogen evolution potential of carbon additives in the lead-carbon electrode, and further enhance the stability of lead-carbon electrode. We have developed several carbon-lead composites for the enhancement of lead-carbon electrodes [6–9]. For the large-scale production of lead-carbon composite additives used in lead-acid battery, we developed a facile sol-gel assisted pyrolysis process for the preparation of oxygen-defective lead oxides deposited lead-carbon composite (RHHPC@PbO<sub>1-x</sub>) used as the negative electrode additives in LCB. RHHPC@PbO<sub>1-x</sub> as an additive shows superior performance. Under PSoC operation, LCB with RHHPC@PbO<sub>1-x</sub> as NAM additive shows a triple cycling life compared with traditional lead-acid battery tested under International Electrotechnical Commission standard (IEC 61427:2005) (shown in Fig. 1). After 6 cycle-sets of test, LCB with RHHPC@PbO<sub>1-x</sub> shows a higher capacity than its initial capacity [10].



**Fig. 2** (a) N<sub>2</sub> adsorption/desorption isotherms and (b) pore size distributions of the lead-carbon electrodes before PSoC tests; (c) N<sub>2</sub> adsorption/desorption isotherms and (d) pore size distributions of the lead-carbon electrodes after PSoC operation. [Reproduced with permission from Ref. \[12\] Copyright 2020, Elsevier.](#)

Lead-carbon electrode	Before PSoC operation			After PSoC operation		
	$S_{\text{BET}}$	$V_{\text{meso}}$	$V_{\text{total}}$	$S_{\text{BET}}$	$V_{\text{meso}}$	$V_{\text{total}}$
	(m <sup>2</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )	(m <sup>2</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )
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 <sub>1-x</sub>	6.81	0.007	0.010	6.50	0.005	0.008

The intrinsic mechanism of RHHPC@PbO<sub>1-x</sub> was studied by SEM and nitrogen-adsorption isotherms. RHHPC@PbO<sub>1-x</sub> enables the uniform deposition of Pb branches, which contributes to the reversible capacity. Secondly, the internal electrochemical active surface area can be maintained by the RHHPC@PbO<sub>1-x</sub> additive, as indicated by the N<sub>2</sub> adsorption and desorption test. The specific surface area of the lead-carbon electrode with RHHPC@PbO<sub>1-x</sub> additive was well maintained by 6.5 m<sup>2</sup> g<sup>-1</sup>, compared to its original value of 6.81 m<sup>2</sup> g<sup>-1</sup> after formation. Lead electrode and lead-carbon electrode with RHHPC additive shows great a huge decrease of specific surface area due to the sulfation (Fig. 2).

The LCB is undergoing a rapid increase in research and commercialization activities. Thus, we need to pay more attention to the aspects of hydrogen evolution, the structural evolution of lead-carbon electrodes during charge-discharge, and the final failure modes of LCB.

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