Accepted Manuscript

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PII: S1572-6657(18)30688-X
DOI: doi:[10.1016/j.jelechem.2018.10.022](https://doi.org/10.1016/j.jelechem.2018.10.022)
Reference: JEAC 12662
To appear in: *Journal of Electroanalytical Chemistry*
Received date: 24 August 2018
Revised date: 1 October 2018
Accepted date: 10 October 2018

Please cite this article as: Jian Yin, Nan Lin, Zheqi Lin, Yue Wang, Jun Shi, Jinpeng Bao, Haibo Lin, Wenli Zhang , Optimized lead carbon composite for enhancing the performance of lead-carbon battery under HRPSoC operation. Jeac (2018), doi:[10.1016/j.jelechem.2018.10.022](https://doi.org/10.1016/j.jelechem.2018.10.022)

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**Optimized lead carbon composite for enhancing the performance of
lead-carbon battery under HRPSoC operation**

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Abstract

The cycle life of lead-carbon battery is greatly restricted by the hydrogen evolution reaction (HER) of lead-carbon electrode. Lead carbon composite, rather than the pure carbon additive, inhibits the HER effectively, and may also strengthen the connection between lead and carbon components of lead-carbon electrode, which contributes to the performance enhancement of lead-carbon battery. In this paper, a novel lead carbon (C/Pb) composite is prepared by electroless plating lead on the rice-husk-based hierarchical porous carbon. The as-prepared C/Pb composite significantly suppresses the HER, and enlarges the electrochemically active surface area of the lead-carbon electrode. As expected, the cycle life of lead carbon battery with the optimized C/Pb composite in negative electrode is more than 11 times of the blank one under high-rate partial state-of-charge (HRPSoC) operation. This performance improvement is attributed to the enhanced interface between lead and carbon, and the inhibition effect on HER of C/Pb composite.

Key words: Lead-carbon battery; Lead carbon composite; Hydrogen evolution; Hierarchical porous structure; Electrochemically active surface area

1 Introduction

Lead-acid battery has been drawing great attention on its application in hybrid electrical vehicle (HEV), due to its unique features including low cost, high safety and good performance at low temperature [1-6]. However, the HEV requires lead-acid battery to be operated under high-rate partial-state-of-charge (HRPSoC) duty, which causes the sulfation of negative electrode and battery failure [7-11]. Lead-carbon battery (LCB) with the addition of proper carbon in the negative electrode has the ability to inhibit sulfation and to prolong the cycle life under HRPSoC operation [11-18]. Unfortunately, the hydrogen evolution reaction (HER) of lead-carbon electrode is accelerated by carbon additive, which restricts the performance of LCB [19]. High rate of HER leads to the water loss of electrolyte and the low energy efficiency of battery. What's more, the generated H_2 gas forces carbon to separate from sponge lead, which destroys the conductive network of lead-carbon electrode [20,21].

In order to inhibit the HER of LCB, numerous efforts have been made to develop electrolyte additives, functionalized carbon materials and electrode additives to improve the over-potential of HER [22-31]. Electrolyte additive changes the interface structure between electrode and electrolyte, subsequently suppressing HER [22-25]. The heteroatoms and functional groups modified on the carbon materials are proved to reduce the HER rate [26-27]. Metal and metallic oxide with high over-potential of HER show remarkable effects on inhibiting HER [28-31]. However, these methods have some drawbacks. The property of electrolyte is changed by the organic additives;

the modification of carbon requires high-temperature treatment and the metallic additives introduce impurities into the LCB.

As is well known, the accelerated HER of lead-carbon electrode is due to the low HER over-potential of carbon [32]. To inhibit HER, the carbon surface exposed to the electrolyte should be reduced [20, 21]. Coating a leady film on the surface of carbon is usually used for this purpose [22, 33-37]. Lead carbon composites can inhibit HER and be beneficial to prolong the cycle life of LCBs. However, the beneficial mechanism of the composite structure of lead and carbon has been neglected. Especially, the lead loading of lead carbon composite and its influence on the electrochemical performance of LCB are urgent to be investigated in detail.

In this paper, a novel lead carbon (C/Pb) composite was prepared to enhance the performance of LCB. The rice husk-based hierarchical porous carbon (RHHPC) with highly porous structure was used as carbon skeleton. Electroless plating method was applied to fabricate this C/Pb composite with a uniformly distributed lead layer. By optimizing the lead loading of C/Pb composite, a balance point has been achieved to get the excellent performance of LCB under HRPSOC operation.

2 Experimental Section

2.1 Preparation

Rice husk-based hierarchical porous carbon (RHHPC) was obtained as described in our previous work [38]. The C/Pb-1 composite was prepared by the same method with 2.40 g lead nitrate and 0.55 g thiourea in the preparation process [39,40]. With the use of 2, 3, 5 times of the lead nitrate and thiourea in the synthesis process, C/Pb-2,

C/Pb-3 and C/Pb-4 were obtained, respectively.

RHHPC and C/Pb films were prepared as the same slurry-coating method described in reference [38]. The carbon films were cut into $1.0 \times 1.0 \text{ cm}^2$ pieces with the mass loading of $4.00 \pm 0.02 \text{ mg cm}^{-2}$. These pieces were pressed to the lead current collector (work area was $1.0 \times 1.0 \text{ cm}^2$, purity > 99.99%) under 5 MPa. LCB with negative active material (NAM) containing 2.00 g RHHPC, 2.01 g C/Pb-1, 2.04 g C/Pb-2, 2.06 g C/Pb-3, 2.19 g C/Pb-4 (ensure the same amount of RHHPC) were marked as RHHPC cell, C/Pb-1 cell, C/Pb-2 cell, C/Pb-3 cell, C/Pb-4 cell. Specific steps of cells' preparation were the same as [40]. The formation process and all tests of the cells were conducted by battery testing system (BTS 5 V/6 A, Shenzhen NEWARE Electronics Co., Ltd., China). After the formation process, each cell was composed of a negative electrode (active mass was $18.0 \pm 0.1 \text{ g}$) and two positive electrodes (active mass was *ca.* 27.0 g), which made the negative electrode a capacity-limiting factor.

2.2 Physical characterization

C/Pb composites were characterized by Scanning Electron Microscope (SEM, SU8020, HITACHI, Japan) and Transmission Electron Microscope (TEM, JEM 1200EX, JEOL, Japan). Elemental analysis was tested by Energy-dispersive X-ray spectroscopy (EDS, Bruker, Germany) combined with SEM and FEI Tecnai G2 S-Twin equipped with Energy-dispersive X-ray (EDS) Detector. After HRPSoC tests, the negative electrodes were also characterized by SEM. Nitrogen adsorption/desorption curves were measured by a surface physical adsorption

instrument (ASAP2010 Micrometrics, USA). Specific surface areas and pore structures were calculated through the Brunauer-Emmett-Teller (BET) and Barrette-Joynere-Halenda (BJH) method, respectively. Resistivity values of the C/Pb composites were tested by a four-point probe method with a semiconductor-powder resistivity instrument (ST-2722, Suzhou lattice, China).

2.3 Electrochemical tests

Electrochemical performance was tested on an electrochemical workstation (PARSTAT 2273, Princeton Applied Research, USA). The counter electrode and the reference electrode were the same as [40]. The linear sweep voltammetry (LSV) was used to evaluate the HER rate. After 30 minutes polarization at -1.20 V, LSV was investigated between the potential range from -1.40 V to -1.10 V (vs. MSE) at a scan rate of 10 mV s^{-1} .

Cell performances were tested on the cell performance tester (BTS 5 V/6 A, NEWARE, China). Chronoamperometry was measured by recording the currents of the fully charged cells at a constant voltage of 2.40 V for 10 h. Electrochemical impedance spectroscopy (EIS) of the cells under open circuit potential with two electrodes system was investigated in the frequency range of 100 kHz~0.1 Hz with a voltage amplitude of 10 mV. The charging plot and the rate performance of the cells were the same as [40]. The steps of HRPSoC operation were the same as reference [11].

3 Results and discussion

The morphologies of the RHHPC and C/Pb composites were characterized by

SEM (Fig. 1). The wide particle size distributions of RHHPC and C/Pb composites, from microns to a hundred microns, are beneficial to integrate RHHPC and C/Pb into the conductive network of NAM [16,41]. Large micron-sized pores derived from vascular bundles of rice husk on the RHHPC and C/Pb composites are good for electrolyte distribution [42]. Notably, the surface of C/Pb-4 is rougher than that of the RHHPC, which may be caused by the deposited lead on C/Pb-4. No apparent differences can be seen between C/Pb composites and RHHPC, which reflects that the deposited lead particles are smaller than micron level. As shown in Fig. 2a-b, the transparent edges of RHHPC indicate the pure carbon phase. On the contrary, many black Pb dots with a diameter of several nanometers are uniformly anchored on the surface of C/Pb-1 in Fig. 2c-d. The element mappings of C/Pb-1 presented in Fig. 2e-h further reveal the uniform distribution of C, O, Pb elements. Additionally, as shown in Table 1, the lead loading of C/Pb-1, C/Pb-2, C/Pb-3, C/Pb-4 are 0.67 wt.%, 2.11 wt.%, 2.93 wt.%, 9.59 wt.%, respectively.

Fig. 1 SEM images (magnified $\times 400$, $\times 3000$, $\times 25000$) of (a) RHHPC, (b) C/Pb-1 composite, (c) C/Pb-2 composite, (d) C/Pb-3 composite, (e) C/Pb-4 composite.

Fig. 2 TEM images of RHHPC (a) $\times 20000$, (b) $\times 70000$, C/Pb-1 composite (c) $\times 20000$, (d) $\times 70000$, (e) Dark-field TEM image and (f) C, (g) O and (h) Pb element mapping of the C/Pb-1 composite.

Table 1

Elemental analysis of the RHHPC and C/Pb composites tested by EDS.

	RHHPC	C/Pb-1	C/Pb-2	C/Pb-3	C/Pb-4
Pb at. %	—	0.04	0.13	0.18	0.63
O at. %	6.74	10.23	14.92	9.76	10.52
C at. %	93.26	89.73	84.96	90.06	88.85
Pb wt. %	—	0.67	2.11	2.93	9.59

Pore structures of the C/Pb composites were further characterized by nitrogen adsorption/desorption. The combined I/IV type isotherms in Fig. 3a demonstrate the 3D structures with rich micropores and mesopores of the RHHPC and C/Pb composites. With the lead loading increasing, specific surface areas, pore volumes and the micropore/mesopore ratios of the C/Pb composites decrease, as shown in Table 2 and Fig. 3b, 3c. The decreased micropore/mesopore ratio is good for electrolyte diffusion and rate performance [43, 44]. The change of pore structure is due to the blockage of pores by the deposited lead. Meanwhile, the resistivity of lead ($2.07 \times 10^{-5} \Omega \text{ cm}$) [45] is significantly lower than that of RHHPC ($0.189 \Omega \text{ cm}$), as shown in Table 2 and Fig. 3d. As expected, increasing lead loading improves the conductivity of C/Pb composite.

Fig. 3 (a) Nitrogen adsorption/desorption isotherms, (b) pore size distributions, (c) micro-structure changes and (d) resistivity values of RHHPC and C/Pb composites.

Table 2

Pore structures and resistivity values of the RHHPC and the C/Pb composites.

	S_{BET}	V_{total}	V_{micro}	V_{meso}	D_{pore}	Resistivity [*]	$V_{\text{meso}}/V_{\text{micro}}$
	($\text{m}^2 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	(nm)	(Ωcm)	
RHHPC	1813.6	1.05	0.52	0.53	2.31	0.19	1.0
C/Pb-1	1192.3	0.71	0.31	0.41	2.39	0.17	1.3
C/Pb-2	964.6	0.58	0.23	0.35	2.41	0.14	1.5
C/Pb-3	778.3	0.49	0.18	0.31	2.51	0.13	1.7
C/Pb-4	669.7	0.42	0.14	0.28	2.51	0.09	2.0

^{*} The resistivity values are tested at 4 MPa.

The HER rates of the C/Pb composites were investigated by LSV and chronoamperometry. Current values of hydrogen evolution increase along with the negative shift of potential in LSV curves (Fig. 4a). At -1.40 V, current values of

RHHPC, C/Pb-1, C/Pb-2, C/Pb-3, C/Pb-4 are -27.5 A g^{-1} , -18.7 A g^{-1} , -8.8 A g^{-1} , -7.6 A g^{-1} , -4.0 A g^{-1} , respectively. It indicates that the hydrogen evolution rate of C/Pb composite decreases with the increase of lead loading on C/Pb composite. And notably, the HER rate of RHHPC is 6 times higher than that of the C/Pb-4 composite. Fig. 4b shows the result of chronoamperometry test, current values of LCBs decrease gradually with time accumulating. After 10 hours, all currents become stable. The current value of the blank cell is the lowest and the cell with RHHPC in the NAM is the highest of all. Both of the LSV and chronoamperometry results show that the HER rate of C/Pb cell decreases with increasing the lead loading of C/Pb composite.

Fig. 4 (a) LSV curves of the RHHPC and C/Pb composites, (b) chronoamperometry of cells at 2.4 V for 10 h.

Positive effects of RHHPC and C/Pb composites on the lead-carbon electrodes were demonstrated by EIS at open circuit potential [46]. The Nyquist plots are shown

in Fig. 5 and simulated by the equivalent circuit presented in Fig. 5b [47]. As shown in Table 3, the ohmic resistance (R_s) values of the lead-carbon electrodes are smaller than the blank one. This suggests good electronic conductivity of the lead-carbon electrodes [42]. Q_f and R_f stand for the non-ideal electric double layer capacitance and the resistance of corrosion layer between grid and the active material. R_{ct} is the charge transfer resistance, corresponding to the Faradaic reaction of Pb/PbSO₄ redox couple. At the equilibrium state, the R_{ct} value is inversely proportional to the kinetic activity of the electrode. Thus, a smaller R_{ct} corresponds to a higher kinetic activity of the lead-carbon electrode [48,49]. The R_{ct} values of the blank, RHHPC and C/Pb-1~4 composite cells are 1.28 Ω , 0.27 Ω , 0.45 Ω , 0.52 Ω , 0.26 Ω , 0.84 Ω , respectively (Table 3). The kinetic activity order from high to low is: C/Pb-3 > RHHPC > C/Pb-1 > C/Pb-2 > C/Pb-4 > blank electrodes. Porous RHHPC and C/Pb composites with high electrochemically active surface areas can enhance the kinetic activity of lead-carbon electrodes. The Q_{dl} indicates the non-ideal electric double layer capacitance of NAM and can be used to compared the electrochemically active surface areas of lead-carbon electrodes [26,49]. With the increasing lead loading of C/Pb composites, Q_{dl} values of C/Pb-1~4 electrodes increase first and then decrease. The Q_{dl} value of C/Pb-3 composite is higher than the other Q_{dl} values. As a summary, with the lead loading of 2.93 wt.%, C/Pb-3 guarantees the high electrochemically active surface area and the enhanced electrochemical kinetics.

Fig. 5 Nyquist plots of the (a) blank cell, (b) RHHPC cell with the equivalent circuit diagram inset, (c) C/Pb-1 cell, (d) C/Pb-2 cell, (e) C/Pb-3 cell, (f) C/Pb-4 cell at open circuit potential.

Table 3

Simulated results of EIS of the lead-carbon cells measured at open circuit potential.

Cell	R_s (Ω)	Q_f ($\Omega^{-1} s^n$)	n	R_f (Ω)	Q_{dl} ($\Omega^{-1} s^n$)	n	R_{ct} (Ω)	χ^2 (10^{-4})
Blank	0.016	1.6	0.95	0.020	10.4	0.66	1.28	4.0
RHHPC	0.012	3.3	0.78	0.007	13.8	0.64	0.27	5.7
C/Pb-1	0.011	6.1	0.60	0.030	12.4	0.75	0.45	9.9
C/Pb-2	0.021	3.7	0.75	0.013	13.2	0.58	0.52	2.7
C/Pb-3	0.008	6.3	0.63	0.020	14.5	0.65	0.26	6.2
C/Pb-4	0.012	5.5	0.62	0.029	11.4	0.80	0.84	8.4

LCBs operated under HEV mode was simulated with the cells under HRPSoC operation [10]. Results show that the cycle numbers of blank, RHHPC, C/Pb-1~4 cells under HRPSoC operation are 887, 4249, 5900, 6855, 10554 and 6186 cycles,

respectively (Fig. 6a). Impressively, the cycle life of C/Pb-3 cell is the longest, which is 11 times longer than that of the blank cell. Within the lead loading of 2.93 wt.%, the cycle life of C/Pb cell increases with increasing the lead loading of C/Pb composite. Beyond the lead loading of 2.93 wt.%, the cycle life of C/Pb cells decrease. This trend is in consistent with the order of electrochemically active surface area tested by EIS. This suggests that the introduced surface areas of C/Pb composites can't represent the extra electrochemical active surface areas of lead-carbon electrodes.

Fig. 6 (a) Cells operated under HRPSoC duty, (b) capabilities and cycle stabilities of the cells in rate capabilities tests.

After HRPSoC operation, rate capabilities of the cells were tested (Fig. 6). Blank cell exhibits the highest discharge capacity at 0.1C₁₀ and the lowest discharge capacity of *ca.* 1.25 Ah at 1C₁. During the cycle process, discharge capacities of the blank cell decrease obviously, while the discharge capacities of C/Pb cells remain stable. The

1C₁ discharge capacity of C/Pb-4 is the highest, *ca.* 1.6 Ah, which is 28% higher than the blank one. Before and after the HRPSoC operation (Fig. 7), the discharge capacities at 1C₁, 0.5C₂, 0.1C₁₀ rates of blank cell decreased by 32.0%, 19.3%, 7.4%; RHHPC cell decreased by 25.6%, 28.1%, 11.7%; C/Pb-3 cell decreased by 8.8%, 2.1%, 0.8% and C/Pb-4 cell decreased by 7.4%, 8.5%, 5.4%, respectively. The changes in discharge capacities demonstrate that the enhanced C/Pb composite structure keeps good charge acceptance and high reversibility of the C/Pb cell [47-49].

Fig. 7 Discharge curves of cells at different discharge rates before and after the HRPSoC operation.

The SEM images of the lead-carbon electrode after HRPSoC operation, as shown in Fig. 8, reveal the relationship between electrode morphology and electrochemical behavior. A dense surface was formed on the blank electrode (Fig. 8a). With the short

time of high-rate charge-discharge currents, the charge transfer rate at the interface of electrode and electrolyte is too slow to get lead sulfate crystals fully converted. These lead sulfate particles continue to grow during the discharge process, resulting in a dense lead sulfate passivating layer on the electrode surface [50-52]. The non-porous surface reduces the chemically active surface area and restricts the electrolyte diffusion in the inner parts of electrode [53]. In this circumstance, charge acceptance of the blank cell degraded rapidly. Therefore, the blank cell exhibited a poor performance under HRPSoC operation and low discharge capabilities in the subsequent test. On the other hand, porous surfaces of the RHHPC and C/Pb-3 electrodes are shown in Fig. 8b and 8c. The additions of RHHPC and C/Pb composites remain the high specific surface areas of lead-carbon electrodes [42]. However, as shown in Fig. 8b, the large cracks between RHHPC and sponge lead are caused by the synthetical effects of the high rate of HER and the poor connection between sponge lead and carbon. Because the active sites on the surface of C/Pb composites only work with both ionic and electronic conductivities, the cracks break down the conductive network of the RHHPC electrode and result in the low discharge capacity. The cracks also suggest that the amount of lead loading on C/Pb composite is the key factor that affects the connection between lead and carbon, and the conductive network in the lead-carbon electrode. Thus, the lead loading of C/Pb composite plays a crucial role in enhancing the electrochemical performance of lead-carbon battery. As presented in Fig. 8c2, with the proper lead loading, the C/Pb-3 composite is firmly embedded in NAM after HRPSoC operation. Hence, C/Pb-3 is

capable of maintaining the lead-carbon electrode with a good conductive network and a high electrochemically active surface area [54]. As a summary, with the lead loading of 2.93 wt.%, C/Pb-3 guarantees the high electrochemical kinetics and its lead-carbon cell exhibits the longest cycle life under HRPSoC operation. Though the HER rate decreases with the increase of lead loading of C/Pb composite, the lead on C/Pb-4 is too much to offer a large electrochemically active surface area for the lead-carbon electrode. Hence, the cycle number of C/Pb-4 cell is less than the C/Pb-3 cell.

Fig. 8 SEM images (magnified $\times 2000$, $\times 5000$) of the (a) blank, (b) RHHPC, (c) C/Pb-3 electrodes after the HRPSoC operation.

Conclusion

A novel C/Pb composite was successfully prepared by electroless plating, where the RHHPC with high specific surface area and porosity was used as carbon skeleton. Results show that by optimizing the C/Pb composite structure with different lead

loading, the HER can be inhibited and the electrochemically active surface area can be enlarged at the same time. The largest electrochemically active surface area can be achieved when the lead loading is 2.93 wt.%. Consequently, its lead-carbon cell exhibits the longest cycle life under HRPSoc operation. With simple preparation, low cost and good electrochemical behavior, the C/Pb composite has the prospect of practical use in advanced LCB.

Acknowledgements

The research group acknowledges the financial support provided by National Natural Science Foundation of China (NO. 21573093) and Guangdong Innovative and Entrepreneurial Research Team Program (NO. 2013C092).

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Graphical abstract

Highlights:

- C/Pb composite inhibits the hydrogen evolution of lead-carbon negative electrode.
- Conductive network of electrode is strengthened by C/Pb composite.
- A balance point of enlarged active surface and strengthened structure is achieved.
- The C/Pb composite improve the reversibility of lead-carbon electrode.
- The cycle life of lead-carbon battery is greatly prolonged by C/Pb composite.