Hierarchical porous carbon@PbO_{1-x} composite for high-performance lead-carbon battery towards renewable energy storage

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ABSTRACT

Utility lead-carbon batteries in renewable energy storage applications require fast charge ability and long-term cycling stability, which introduces a fundamental problem that how to improve the electrode kinetics and cycling stability of lead-carbon electrode. Herein, we present an oxygen-deficient PbO decorated rice-husk-based hierarchical porous carbon (RHHPC@PbO_{1-x}) composite as an effective additive of negative electrode in lead-carbon battery. The RHHPC@PbO_{1-x} composite was prepared from a facile sol-gel/annealing method. The obtained RHHPC@PbO_{1-x} composite and the lead-carbon electrode with RHHPC@PbO_{1-x} additives were characterized by various physicochemical methods, such as scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and multiple electrochemical methods. The RHHPC@PbO_{1-x} composite enhances the electrochemical active surface area and strengthens the structural stability of lead-carbon electrode, which improves the electrode kinetics and the cycling stability of lead-carbon negative electrode. As a result, the cycling life of a 2 V/4 Ah valve-regulated lead-carbon battery with RHHPC@PbO_{1-x} composite additives exhibited a lifespan of 900 cycles (triple of the blank battery). Our work gives an insight for interphase and porosity tuning of lead-carbon additives used in lead-carbon battery. Based on the existing mature production facilities of lead-acid battery, it is promising for this RHHPC@PbO_{1-x} additive to be used in commercial lead-carbon batteries for renewable energy storage.

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1. Introduction

The demand for the storage of electricity from renewable energy sources has stimulated the fast development of battery technology with low cost and long lifespan [1–3]. Lead-acid battery is the most mature and the cheapest (cost per watt-hour) battery among all the commercially available rechargeable batteries [4]. In renewable energy storage, lead-acid battery is operated under partial state of charge (PSoC). In PSoC, lead negative electrode gradually becomes sulfated, and its capacity decreases rapidly. Various carbon additives inhibit the sulfation of Pb negative electrode [5], due to the improved conductivity [6–8], increased electrochemical active surface area [9–11], enhanced electrolyte diffusion [12,13], and increased double-layer capacitive effects [8,14,15], etc. In consideration of the remarkable cycling life of carbon-enhanced lead-acid battery operated under PSoC operation,

the terminology of lead-carbon battery is proposed to introduce a lead-acid battery coupled with a long-life carbon-enhanced lead-carbon negative electrode [16]. Despite the significant performance improvement achieved by adding carbon additives in negative electrode, carbon additives induce a high-rate hydrogen evolution reaction (HER) which results in serious water loss and low energy efficiency during charge-discharge [13,17,18]. Furthermore, the release of hydrogen bubbles could physically destroy the conductive network of lead-carbon electrode and separate the lead and carbon components in lead-carbon electrode [19–21]. As a result, the HER hampers the lifespan enhancement of lead-carbon battery [11,22].

Chemically decorating carbon with hydrophobic molecules [23,24], heteroatoms [25–27], and metal/metal oxides with high HER overpotential [28–30] are demonstrated as effective methods to inhibit the HER of lead-carbon electrodes. Among these methods, compositing carbon with lead species not only suppresses the HER but also could enhance the affinity between lead and carbon components in the lead-carbon electrode [31–33]. Since Pb is of high HER overpotential and is the major component of negative electrode, decorating carbon with lead is one of the best methods to enhance the stability of lead-carbon electrode [34–36] while do not introduce impurities. Nevertheless, in previous studies, the micropore-dominated pore structure, the uneven Pb distribution, and the low porosity of the resulting lead-carbon com-

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posite restrict the performance enhancement of lead-carbon electrode [16]. In recent years, hierarchical porous carbon has drawn great attention due to its high specific surface area, high outer surface (high meso- and macro-pore ratio) area and hierarchical porous structure [37–39]. In a lead-carbon battery system, carbon additives with hierarchical pores can enlarge the electrochemical active surface area for the growth of energetic Pb branches [40], which significantly enhances the electrode kinetics of Pb/PbSO₄ redox couple [11,41]. Besides, Pb species deposited on carbon surface could enhance the affinity between energetic Pb branches and carbon additives. Therefore, it is of significance to develop a high-surface-area lead-carbon composite with homogeneous Pb deposited on the hierarchical porous carbon for lead-carbon battery.

Rice-husk-based hierarchical porous carbon (RHHPC) is a kind of high-surface-area porous carbon with a three-dimensional hierarchical pore structure [42]. In our previous study, we have demonstrated that RHHPC is beneficial to inhibiting the sulfation of lead electrode and enlarging the electrochemical active surface area [43]. Nevertheless, many technical problems remain for utility applications. On the one hand, the HER rate of RHHPC needs to be further inhibited by uniform Pb coating. On the other hand, considering the large-scale applications of carbon-based additives in lead-carbon battery, we need to produce lead-carbon composite in a facile, large-scale way which can be easily industrialized. In this paper, a sol-gel method was introduced to prepare the precursor of RHHPC@PbO_{1-x} composite. Under annealing process, robust lead-carbon interphase was achieved by annealing-assisted carbon reduction reaction. Lead-carbon battery with RHHPC@PbO_{1-x} composite in negative active materials (NAM) exhibited superior cycling stability in simulated test protocols for renewable energy storage. This work gives an insight for interphase and structural tuning of lead-carbon additives used in lead-carbon battery.

2. Experimental section

2.1. Preparation of RHHPC@PbO_{1-x} composite by sol-gel/annealing

RHHPC was obtained as described in our previous work [42]. A modified sol-gel method [44] combined with annealing was used to prepare RHHPC@PbO_{1-x} composite (Fig. 1a). Specifically, 10 g RHHPC was soaked in 100 mL 19 wt % lead acetate solution with vigorous stirring for 10 min to form a homogeneous solution. 100 mL 21 wt % citric acid solution was added in above solution stirring for 2 h. Gel was formed and dried by solvent evaporation in a 120 °C air-flow oven. Afterward, the precursor was heat-treated at 500 °C for 1 h in a muffle furnace under a heat ramping rate of 10 °C min⁻¹. As the temperature increased to 500 °C, lead citrate was transformed into carbon and PbO_{1-x}. Thus, the RHHPC@PbO_{1-x} composite with homogeneous PbO_{1-x} deposition was formed in this facile sol-gel/annealing preparation.

The detailed preparation procedures and other necessary additives of lead-carbon cells can be found in our previous publications [22] in which negative pastes contain 1.00 g RHHPC or 1.19 g RHHPC@PbO_{1-x} composite (to ensure the equal mass loading of RHHPC in NAM) with respective to 100 g leady oxide. Lead-carbon cells using RHHPC and RHHPC@PbO_{1-x} additives were denoted as RHHPC and RHHPC@PbO_{1-x} cells, respectively. A blank cell with no RHHPC additives was also made as a reference. The lead-carbon electrodes (geometry size of 40.0 mm × 68.0 mm × 1.5 mm) were assembled into a full battery (Fig. 1b–d). All cells were made by three negative electrodes and two commercial positive electrodes. Small-sized lead-carbon electrodes (geometry size of 6.0 mm × 8.0 mm × 1.5 mm) were made for electrochemical characterizations. Commercial absorbent glass mat (AGM) was used as separator and a 5 mol L⁻¹ sulfuric acid solution was used as the electrolyte. The formation and all the electrochemical tests of the cells were conducted on a BTS battery testing system (5 V/6 A, Shen-

Fig. 1. (a) Schematic diagram for the synthesis of RHHPC@PbO_{1-x} composite. (b) Lead oxide powder. (c) Lead alloy grid, lead-carbon electrode, and lead dioxide electrode before formation (from left to right). (d) Digital photograph of an assembled 2 V/4 Ah lead-carbon battery.

zhen NEWARE, China) using the methods described in our previous publications [45].

2.2. Physicochemical characterization and calculation

Morphologies of the additives and lead-carbon electrodes were characterized by a Scanning Electron Microscope (SEM, SU8020, Hitachi, Japan) and a Transmission Electron Microscope (TEM, FEI Tecnai G2 S-Twin, USA). Elemental analysis was tested by energy-dispersive X-ray spectroscopy (EDS, Bruker, Germany) combined with SEM and FEI Tecnai G2 S-Twin equipped with EDS Detector. The crystal structure of RHHPC@PbO_{1-x} composite was determined by powder X-ray diffraction (XRD) with Cu α radiation on a Rigaku D/Max 2500 diffractometer. X-ray photoelectron spectroscopy (XPS) data were obtained on an ESCALAB 250 X-ray photoelectron spectrometer with an Mg α excitation source. Nitrogen adsorption/desorption isotherms were measured by a nitrogen adsorption/desorption analyzer (3H-2000PM2, Beishide, China). The specific surface areas and pore size distributions of carbon additives and lead-carbon electrodes were evaluated by the Brunauer-Emmett-Teller (BET) and Barrette-Joyner-Halenda (BJH) models, respectively.

2.3. Electrochemical test and evaluation

Three-electrode electrochemical tests: The counter electrode was a commercial paste-type PbO₂ electrode, and the reference electrode was mercurous sulfate electrode [22,46]. The HER rates of lead-carbon electrodes were evaluated by linear scan voltammetry (LSV), steady-state polarization, and electrochemical impedance spectroscopy (EIS). After the formation, a 20 min negative polarization at -1.20 V was conducted to ensure the fully charged state of the lead-carbon electrodes. LSV was tested within the potential range from -1.50 V to -1.20 V at a scan rate of 5 mV s⁻¹. Steady-state galvanostatic polarization of the lead-carbon electrodes were tested stepwise with constant currents of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, and 50 mA after 20 min. The voltages were recorded by a multimeter. EIS was tested at -1.30 V and open circuit potential (OCP) in the frequency range of 100 kHz–100 mHz with a voltage amplitude of 5 mV. Cyclic voltammetry (CV) tests were carried out within the potential range from -1.50 V to -0.60 V at scan rates of 1, 5 and 10 mV s⁻¹, respectively. All the electrochemical tests (CV, LSV, and EIS) were conducted on a Parstat 2273 electrochemical workstation (Ametek, USA) in ambient environment.

Battery electrochemical performances tests: Galvanostatic charge-discharge tests were carried out to evaluate the electrochemical performances of lead-carbon electrodes. After formation, two negative electrodes were removed, leaving one negative and two positive electrodes, thus making the negative electrode a capacity-limiting factor. The cells were discharged at currents of 0.1C₁₀, 0.2C₅ 1C₁, and 0.1C₁₀. In the deep charge/discharge cycling under PSoC operation, cells were tested within 0–60% SoC [40,47] using the following protocols: (1) Fully charge the cells, and discharge cells to 1.8 V at 0.1C₁₀ rate; (2) After resting for 5 h, charge the cells at 0.1C₁₀ rate with a voltage limit of 2.4 V for 6 h; (3) Discharge the cells at 0.1C₁₀ rate to 1.8 V; (4) Repeat step (2) and (3) for 4 times, then examine the capacity of cells with step (1); (5). Repeat step (4) to continue the deep charge/discharge cycling under PSoC operation.

The hand-made blank and RHHPC@PbO_{1-x} cells (4.0 Ah of 2 h' capacity with balanced negative and positive capacities) were also made and tested according to the Chinese National Standard (GB/T 22473-2008) (with equal authenticity to the International Electrotechnical Commission standard, IEC 61427:2005). Cycling test ends when the capacity of the lead-carbon cell drops below 80% of its initial discharge capacity after one cycle set [48]. All the electrochemical performances of batteries were tested on a BTS battery testing system (5 V/6 A, Shenzhen NEWARE, China).

3. Results and discussion

RHHPC and RHHPC@PbO_{1-x} possessed macropores with various sizes as shown in Fig. S1 (see Supporting Information) and Fig. 2a–b. The macropores in RHHPC and RHHPC@PbO_{1-x} composite are beneficial for fast ionic transport in the NAM [42]. SEM, TEM and High-angle annular dark-field (HAADF) images demonstrated that nano-size PbO_{1-x} particles were uniformly deposited in RHHPC@PbO_{1-x} composite (Fig. 2c–e). Elemental mappings tested by EDS illustrated the uniform distribution of Pb element on the RHHPC@PbO_{1-x} composite (Fig. 2e). XRD pattern of precursor gel showed the typical hump peaks of amorphous carbon centering around 24° (002) and 44° (100), while the peaks of lead citrate are too weak to be identified (Fig. S2). By contrast, in the XRD pattern of the annealed RHHPC@PbO_{1-x} composite, the new diffraction peaks of β -PbO (JCPDS No. 38-1477) and Pb (JCPDS No. 04-0686) were obvious (Fig. 2f). The chemical compositions and oxidation states of RHHPC@PbO_{1-x} composite were analyzed by XPS spectra (Fig. 2g and h). XPS survey spectrum corroborates the existence of C, O and Pb elements, which matches well with the EDS result. High-resolution spectra of Pb 4f centering around 138.6 eV and 143.4 eV can be differentiated into two pair of peaks of Pb (136.9 eV and 141.7 eV) and PbO (138.6 eV and 143.4 eV) [49–52]. Due to the deficiency of oxygen in PbO, the above lead-carbon composite is named as RHHPC@PbO_{1-x} composite. Furthermore, since Pb was obtained by carbon reduction of PbO in the annealing process, an enhanced, stable three-phase heterogeneous composite structure (RHHPC/Pb/PbO) was formed between PbO and RHHPC. In this three-phase heterogeneous composite structure, RHHPC/Pb acts as interphase could enhance the structural stability of RHHPC@PbO_{1-x} composite. The enhanced lead-carbon interphase could contribute to inhibiting HER and building the conductive network between sponge lead and RHHPC@PbO_{1-x} composite in a formed lead-carbon electrode. The EDS analysis (Figs. S3 and S4) indicated a lead loading of 19.3 wt % in RHHPC@PbO_{1-x} composite.

N₂ adsorption/desorption isotherm was used to identify the pore structure of RHHPC@PbO_{1-x} composite. As shown in Fig. 3a, the isotherms of RHHPC and RHHPC@PbO_{1-x} composite belonged to the combined I/IV type according to the International Union of Pure and Applied Chemistry classification, indicating that RHHPC and RHHPC@PbO_{1-x} composite possess micro/mesoporous structures. Because in RHHPC@PbO_{1-x} some PbO_{1-x} particles are embedded in the pores of RHHPC, the pore volume and specific surface areas of RHHPC@PbO_{1-x} composite (0.66 cm³ g⁻¹ and 1111.3 m² g⁻¹) are lower than those of the RHHPC (1.03 cm³ g⁻¹ and 1810.2 m² g⁻¹), as shown in Table S1. The relatively high pore volume and specific surface area of RHHPC@PbO_{1-x} composite could benefit the electrode kinetics of Pb/PbSO₄ redox, and subsequently improve the charge acceptance of lead-carbon electrode [11].

HER is the main factor that limits the cycling stability of lead-carbon electrode. The HER rates, tested by LSV, were shown in the ascending order of blank < RHHPC@PbO_{1-x} < RHHPC electrodes (Fig. 4a). Besides LSV, we have made a quantitative comparison of HER gravimetric current through steady-state polarization technique (Fig. 4b). At -1.50 V, the HER current densities of blank, RHHPC, RHHPC@PbO_{1-x} electrodes were -6.5, -72.5 and -40.5 mA g⁻¹, respectively. The different HER kinetics of lead-carbon electrodes were further analyzed by the EIS at -1.30 V (Fig. S5) and fitted with an equivalent circuit (Fig. S5) [40]. The simulated results are presented in Table S2. The RHHPC@PbO_{1-x} electrode exhibited a higher charge transfer resistance (45.7 Ω) than the RHHPC electrode (29.6 Ω), which is in accordance with the results of LSV and steady-state polarization. The above results suggest that the RHHPC@PbO_{1-x} composite with robust lead-carbon interphase slows down the HER rate of the lead-carbon electrode.

CV curves reveal the different electrochemical behaviors of lead-carbon electrodes (Figs. 4c and S6). Compared with the blank electrode, the shifts of redox peaks towards the scanning directions indicate the higher porosity of RHHPC and RHHPC@PbO_{1-x} electrodes. The ab-

Fig. 2. Physicochemical characterization of RHHPC@PbO_{1-x} composite. (a, b) SEM images, (c, d) TEM images and (e) the HAADF image and elemental mappings of C, O and Pb of RHHPC@PbO_{1-x} composite. (f) XRD patterns and (g) XPS survey spectrum for RHHPC and RHHPC@PbO_{1-x} composite. (h) High-resolution XPS spectrum of Pb 4f of RHHPC@PbO_{1-x} composite.

Fig. 3. (a) N₂ absorption/desorption isotherms and (b) pore size distributions of the RHHPC and RHHPC@PbO_{1-x} composite.

solute values of redox peak currents of the RHHPC and RHHPC@PbO_{1-x} electrodes were higher than the blank electrode. Higher peak current densities imply higher electrochemically active surface areas for Pb²⁺ deposition resulting from the addition of RHHPC and RHHPC@PbO_{1-x} composite. As shown in Table S3, the reversibility of Pb/PbSO₄ redox couple of lead-carbon electrode was compared with the absolute ratio of reduction and oxidation peak current ($|I_R|/|I_O|$). The $|I_R|/|I_O|$ values of blank, RHHPC and RHHPC@PbO_{1-x} electrodes were 0.45, 0.66 and 0.70, respectively. The highest $|I_R|/|I_O|$ ratio of the RHHPC@PbO_{1-x} electrode corresponds to the best reversibility of Pb/PbSO₄ redox of all lead-carbon electrodes.

EIS was also used to analyze the electrochemical kinetics of the lead-carbon electrodes, as shown in Fig. 4d. The equivalent circuit diagram in Fig. S6d was used for simulation [40]. As presented in Table 1, the R_{ct} values of lead-carbon electrodes were smaller than that of the blank electrode (3.0 Ω). The smallest R_{ct} value of all belongs to

the RHHPC@PbO_{1-x} electrode (1.8 Ω), which implies its fast kinetics of Pb/PbSO₄ redox couple. The Q_{dl} value corresponds to the electrochemical active surface area of lead-carbon electrode [22]. Although the specific surface area of RHHPC was higher than that of the RHHPC@PbO_{1-x} composite, the highest Q_{dl} value belongs to the RHHPC@PbO_{1-x} electrode (0.114 Ω⁻¹ sⁿ) rather than RHHPC electrode (0.095 Ω⁻¹ sⁿ). The reason is elaborated as follows. The enhanced lead-carbon interphase of RHHPC@PbO_{1-x} composite establishes the effective connection between RHHPC@PbO_{1-x} composite and sponge lead, which improves the utilization of hierarchical pores of lead-carbon electrode for the deposition of energetic lead. In addition, the R_s values of lead-carbon electrodes were lower than that of the blank electrode, which suggests the beneficial effects for electrolyte adsorption of RHHPC@PbO_{1-x} composite [6,40].

Rate capabilities and the cycling performances of lead-carbon cells in deep charge/discharge cycling under PSoC operation were

Fig. 4. Electrochemical performances of lead-carbon electrodes. (a) LSV curves. (b) Steady-state polarization curves. (c) CV curves at a scan rate of 5 mV s^{-1} . (d) Nyquist plots tested at OCP.

Table 1

The simulated EIS results of lead-carbon electrodes at OCP.

Cells	R_s (Ω)	Q_f ($\Omega^{-1} \text{ s}^n$)	n	R_f (Ω)	Q_{dl} ($\Omega^{-1} \text{ s}^n$)	n	R_{ct} (Ω)	χ^2 (10^{-4})
Blank	0.32	0.030	0.70	0.20	0.047	0.86	3.0	3.2
RHHPC	0.25	0.020	0.78	0.09	0.095	0.70	2.2	3.6
RHHPC@PbO _{1-x}	0.29	0.040	0.74	0.09	0.114	0.71	1.8	2.0

tested. Fig. 5a shows the same discharge capacities of ca. 2.50 Ah at $0.1C_{10}$ rate for all the cells at the beginning of cycling. When the discharge rate was switched back to $0.1C_{10}$, the discharge capacities recovered to ca. 2.50 Ah, which suggests the excellent stabilities of lead-carbon cells. The discharge capacity of RHHPC@PbO_{1-x} cell (1.64 Ah) at $1C_1$ rate was significantly higher than that of the blank (0.94 Ah) and RHHPC (1.35 Ah) cells. The high capacity of RHHPC@PbO_{1-x} at $1C_1$ cell is in agreement with the results from CV and EIS. The RHHPC@PbO_{1-x} composite with enhanced lead-carbon interphase improves the utilization of its hierarchical pores, which enlarges the electrochemically active surface area of lead-carbon electrode effectively.

Fig. 5b–d shows the cycling performance of cells in deep charge/discharge cycling under PSoC operation [40,47]. Because the 100% deep of discharge and the 5 h's rest at 0% SoC cause serious sulfation problem, the discharge capacities of all cells decrease quickly. In the 81st cycle, the discharge capacity of blank cell was lower than 80% of the capacity at the 1st cycle, while the discharge capacity of RHHPC cell at 136th cycle decreased to 80% that of the capacity at the 1st cycle. After 350 cycles, the RHHPC@PbO_{1-x} cell displayed a capacity as high as 96.5% of the discharge capacity at its 1st cycle. What is more, the cycling life of RHHPC@PbO_{1-x} cell was fourfold of the blank cell, and twice of the RHHPC cell. The above result verifies the good effect of RHHPC@PbO_{1-x} composite with enhanced lead-carbon interphase on suppressing HER, strengthening the conductive network be-

tween RHHPC@PbO_{1-x} composite and sponge lead, and enlarging the electrochemical active surface area for Pb deposition. Furthermore, the conductive network makes full use of the hierarchical pores of the RHHPC@PbO_{1-x} electrode. Both of the enhanced lead-carbon interphase and the hierarchical pores of RHHPC@PbO_{1-x} composite contribute to the excellent performances of RHHPC@PbO_{1-x} cell. Furthermore, fast declines in the charge acceptance of RHHPC and blank cells as well as the excellent charge acceptance of RHHPC@PbO_{1-x} cell were observed (Fig. S7), which agrees well with the EIS and CV results.

The negative electrodes before and after the PSoC cycling test were characterized by XRD, SEM and N_2 adsorption/desorption techniques. As shown in Fig. 6, the XRD pattern of blank electrode showed typical peaks of Pb and PbSO₄ before the PSoC cycling tests, while the RHHPC and RHHPC@PbO_{1-x} electrodes only showed Pb peaks. The above results suggest that RHHPC and RHHPC@PbO_{1-x} composite expedites the formation process of lead-carbon electrodes. After PSoC operation, the RHHPC@PbO_{1-x} electrode had the least amount of PbSO₄ among all lead-carbon electrodes, while the RHHPC electrode had a larger amount of PbSO₄. SEM images in Fig. 7 reveal the morphology changes of negative electrode. Before PSoC cycling, the blank electrode showed a majority of block particles, while the RHHPC and RHHPC@PbO_{1-x} electrodes mainly possessed carrot-shaped Pb branches. Hence, RHHPC and RHHPC@PbO_{1-x} composite contribute to the high specific surface area of NAM, which enhances the charge ac-

Fig. 5. (a) Rate capabilities and the performances under PSoc operation of the (b) blank, (c) RHHPC and (d) RHHPC@PbO_{1-x} cells.

Fig. 6. The XRD patterns of lead-carbon electrodes (a) before tests and (b) after the PSoc operation.

ceptance of NAM. After cycling test, a passive layer of PbSO₄ was formed on the surface of blank electrode. Obviously, some RHHPC particles were separated from the sponge lead in the RHHPC electrode due to the severe HER reaction. Different from blank electrode and RHHPC electrodes, RHHPC@PbO_{1-x} electrode remained the high specific surface area of NAM without separation phenomenon, which is in accordance with the pore parameters tested by N₂ adsorption/desorption isotherms (Fig. S8 and Table S4). Compared with RHHPC@PbO_{1-x} electrode, the relatively low specific surface area and pore volume of RHHPC electrode result from the poor connection between RHHPC

and sponge lead. What is more, apparently, RHHPC@PbO_{1-x} electrode exhibit an integrated lead-carbon composite morphology, which is due to that the strengthened RHHPC/C interphase enables the growth of Pb energetic branches. The integrated lead-carbon structure enables the long-term cycling stability of lead-carbon electrode. In addition, according to the current density distribution, the most polarized region as well as the part which is the part most likely get sulfated of the negative electrode focus on the bottom [53–56]. Hence, the detached part on the bottom represents bad charge acceptance of blank and RHHPC electrodes. The compactness of RHHPC@PbO_{1-x} electrode is well pre-

Fig. 7. SEM images of (a, b) blank, (c, d) RHHPC and (e, f) RHHPC@PbO_{1-x} electrodes before (a, c and e) and after PSOC cycling (b, d, and f).

served (Fig. S9) because of its robust lead-carbon interphase and the unique hierarchical pore structure.

As a demonstration for the storage of electricity generated from renewable energy from photovoltaics and wind, the lead-carbon full batteries (4.0 Ah of 10 h' capacity) were tested according to the Chinese National Standard (GB/T 22473-2008). The cycling performances of lead-carbon full batteries are shown in Fig. 8. The blank battery ran only 2 cycle sets (300 cycles) before the discharge capacity drops to 2.97 Ah (less than 80% of 4.0 Ah). The RHHPC@PbO_{1-x} battery completed 6 cycle sets (900 cycles) with a discharge capacity of 5.39 Ah in the end (Fig. S10a). The cycling number of RHHPC@PbO_{1-x} battery was three times that of the blank battery. Compared with the charge voltage in the standard GB cycling test, blank battery exhibited serious polarization phenomenon while the RHHPC@PbO_{1-x} battery showed steady charge-discharge behavior (Figs. 8 and S10b). To highlight the unique performances of RHHPC@PbO_{1-x} composite, we also compared the specific capacities and cycling stabilities between the lead-carbon cells made by our RHHPC@PbO_{1-x} and other additives in literatures (Table 2). Actually, the capacity retention of RHHPC@PbO_{1-x} cell is the best among the references. There is no doubt that the RHHPC@PbO_{1-x} composite can improve the cycling life of lead-carbon battery towards renewable energy storage.

4. Conclusion

A novel RHHPC@PbO_{1-x} composite with hierarchical pores has been prepared by a facile combined sol-gel/annealing method. The 2 V/4 Ah valve-regulated lead-carbon battery with RHHPC@PbO_{1-x} composite additive in the negative electrode achieved 900 cycles' cycling life (triple of the blank battery) in the Chinese national standard (GB/T 22473-2008) test. The excellent performance of RHHPC@PbO_{1-x} cell originates from the unique lead-carbon interphase of RHHPC@PbO_{1-x} composite, which not only inhibits the HER but also enlarges the electrochemical active surface and strengthens the connection between lead and carbon. The lead-carbon battery facilitated by RHHPC@PbO_{1-x} composite has the potential to meet the requirements of low-cost, large-scale renewable energy storage technology.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work.

Fig. 8. The charge/discharge voltage profiles and the Coulombic efficiencies of (a) blank and (b) RHHPC@PbO_{1-x} 2 V/4 Ah valve-regulated lead-carbon battery in the standard GB cycling test.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.energy.2019.116675>.

Table 2
Comparison of the performances between RHHPC@PbO_{1-x} and other additives in literatures.

Additives	Specific capacity			Cycling stability			Ref
	Current	Cycling Number	Capacity (mAh g ⁻¹)	Current	Cycles	Retention	
SDC ^a	—	—	—	I ₁₀	30	93%	[10]
Nano-Pb/AC ^a	I ₃	—	102.6	100 mA g ⁻¹	60	50%	[57]
MWCNT ^a	—	—	—	I ₁₀	205	87%	[58]
0.005%PASP ^{a,*}	—	—	—	I ₁₀	31	95%	[59]
0.005%PASP ^a	—	—	—	I ₁	200	87%	[59]
CSGE ^{a,*}	—	—	—	I ₁₀	31	86%	[47]
CSGE ^a	—	—	—	I ₁₀	208	60%	[47]
RHC ^{b,*}	I ₂	1	75	I ₂	300	69%	[40]
Pb/Carbon ^{b,*}	I ₁₀	1	128	I ₁₀	90	63%	[22]
N-doped Carbon ^b	—	—	—	I ₁	150	70%	[60]
RHHPC@PbO _{1-x} ^{b,c}	I ₁₀	246	147.4	I ₁₀	351	96.4%	This work

Notes.

^a The additives for electrolyte.

^b The additives for lead negative electrodes.

^c Tested under 100%DoD in PSoC operation.

References

- [1] JOG Posada, AJR Rennie, SP Villar, VL Martins, J Marinaccio, A Barnes, et al. Aqueous batteries as grid scale energy storage solutions. *Renew Sustain Energy Rev* 2017;68:1174–1182. doi:10.1016/j.rser.2016.02.024.
- [2] P Kurzweil, J Garche. Overview of batteries for future automobiles. Lead-acid batter. *Futur. Automob.* Elsevier B.V.; 2017. doi:10.1016/B978-0-444-63700-0.00002-7.
- [3] W Zhang, F Zhang, F Ming, HN Alshareef. Sodium-ion battery anodes: status and future trends. *EnergyChem* 2019;1:100012. doi:10.1016/j.enchem.2019.100012.
- [4] T Kousskou, P Bruel, A Jamil, T El Rhafiki, Y Zeraoui. Energy storage: applications and challenges. *Sol Energy Mater Sol Cells* 2014;120(Part A):59–80. doi:10.1016/j.solmat.2013.08.015.
- [5] PT Moseley, RF Nelson, AF Hollenkamp. The role of carbon in valve-regulated lead-acid battery technology. *J Power Sources* 2006;157:3–10. doi:10.1016/j.jpowsour.2006.02.031.
- [6] X Zou, Z Kang, D Shu, Y Liao, Y Gong, C He, et al. Effects of carbon additives on the performance of negative electrode of lead-carbon battery. *Electrochim Acta* 2015;151:89–98. doi:10.1016/j.electacta.2014.11.027.
- [7] SM Kumar, S Ambalavanan, S Mayavan. Effect of graphene and carbon nanotubes on the negative active materials of lead acid batteries operating under high-rate partial-state-of-charge operation. *RSC Adv* 2014;4:36517. doi:10.1039/C4RA06920J.
- [8] A Jaiswal, SC Chalasani. The role of carbon in the negative plate of the lead-acid battery. *J Energy Storage* 2015;1:15–21. doi:10.1016/j.jest.2015.05.002.
- [9] D Pavlov, P Nikolov, T Rogachev. Influence of expander components on the processes at the negative plates of lead-acid cells on high-rate partial-state-of-charge cycling. Part I: effect of lignosulfonates and BaSO₄ on the processes of charge and discharge of negative plates. *J Power Sources* 2010;195:4435–4443. doi:10.1016/j.jpowsour.2009.11.060.
- [10] M Saravanan, M Ganesan, S Ambalavanan. An in situ generated carbon as integrated conductive additive for hierarchical negative plate of lead-acid battery. *J Power Sources* 2014;251:20–29. doi:10.1016/j.jpowsour.2013.10.143.
- [11] W Zhang, H Lin, H Lu, D Liu, J Yin, Z Lin. On the electrochemical origin of the enhanced charge acceptance of the lead-carbon electrode. *J Mater Chem A Mater Energy Sustain* 2015;3. doi:10.1039/c4ta05891g.
- [12] J Xiang, P Ding, H Zhang, X Wu, J Chen, Y Yang. Beneficial effects of activated carbon additives on the performance of negative lead-acid battery electrode for high-rate partial-state-of-charge operation. *J Power Sources* 2013;241:150–158. doi:10.1016/j.jpowsour.2013.04.106.
- [13] PT Moseley, DAJ Rand, K Peters. Enhancing the performance of lead-acid batteries with carbon - in pursuit of an understanding. *J Power Sources* 2015;295:268–274. doi:10.1016/j.jpowsour.2015.07.009.
- [14] S Meenakum, P Termsuksawad, S Phiboonkulsumrit. Effects of carbon structure and mixing sequence in an expander on the capacity of negative electrodes in a traction battery. *J Mater Eng Perform* 2015;24:45–52. doi:10.1007/s11665-014-1269-0.
- [15] G Li, W Lei, D Luo, YP Deng, D Wang, Z Chen. 3D porous carbon sheets with multidirectional ion pathways for fast and durable lithium-sulfur batteries. *Adv Energy Mater* 2018;8:1702381. doi:10.1002/aenm.201702381.
- [16] Y Hu, J Yang, J Hu, J Wang, S Liang, H Hou, et al. Synthesis of nanostructured PbO/C composite derived from spent lead-acid battery for next-generation lead-carbon battery. *Adv Funct Mater* 2018;1705294:1705294. doi:10.1002/adfm.201705294.
- [17] D Pavlov, P Nikolov. Capacitive carbon and electrochemical lead electrode systems at the negative plates of lead-acid batteries and elementary processes on cycling. *J Power Sources* 2013;242:380–399. doi:10.1016/j.jpowsour.2013.05.065.
- [18] D Pavlov, P Nikolov. Lead-carbon electrode with inhibitor of sulfation for lead-acid batteries operating in the HRPSOC duty. *J Electrochem Soc* 2012;159:A1215–A1225. doi:10.1149/2.035208jes.
- [19] PT Moseley, DAJ Rand, B Monahov. Designing lead-acid batteries to meet energy and power requirements of future automobiles. *J Power Sources* 2012;219:75–79. doi:10.1016/j.jpowsour.2012.07.040.
- [20] K Peters, DAJ Rand, PT Moseley. Performance-enhancing materials for lead-acid battery negative plates. Elsevier I; 2017. doi:10.1016/B978-0-444-63700-0.00007-6.
- [21] PT Moseley, DAJ Rand, A Davidson, B Monahov. Understanding the functions of carbon in the negative active-mass of the lead-acid battery: a review of progress. *J Energy Storage* 2018;19:272–290. doi:10.1016/j.jest.2018.08.003.
- [22] J Yin, N Lin, W Zhang, Z Lin, Z Zhang, Y Wang, et al. Highly reversible lead-carbon battery anode with lead grafting on the carbon surface. *J Energy Chem* 2018;27:1674–1683. doi:10.1016/j.jchem.2018.03.002.
- [23] MA Deyab. Hydrogen evolution inhibition by L-serine at the negative electrode of a lead-acid battery. *RSC Adv* 2015;5:41365–41371. doi:10.1039/c5ra05044h.
- [24] Y Zhang, X Liu, J Cai, R Zhao, Z Li, H Chen. Influence of sodium polyaspartate added to the negative active material on the electrochemical behavior of lead-acid batteries. *Ionics* 2015;21:2693–2700. doi:10.1007/s11581-015-1446-7.
- [25] F Wang, C Hu, J Lian, M Zhou, K Wang, J Yan, et al. Phosphorus-doped activated carbon as a promising additive for high performance lead carbon batteries. *RSC Adv* 2017;7:4174–4178. doi:10.1039/C6RA26093D.
- [26] B Hong, X Yu, L Jiang, H Xue, F Liu, J Li, et al. Hydrogen evolution inhibition with diethylenetriamine modification of activated carbon for a lead-acid battery. *RSC Adv* 2014;4:33574–33577. doi:10.1039/C4RA04245J.
- [27] L Wang, H Zhang, G Cao, W Zhang, H Zhao, Y Yang. Effect of activated carbon
- [28] L Zhao, M Zhou, Y Shao, D Wang. Hydrogen evolution behavior of electrochemically active carbon modified with indium and its effects on the cycle performance of valve-regulated lead-acid batteries. *RSC Adv* 2014;4:44152–44157. doi:10.1039/C4RA04670F.
- [29] L Zhao, B Chen, D Wang. Effects of electrochemically active carbon and indium (III) oxide in negative plates on cycle performance of valve-regulated lead-acid batteries during high-rate partial-state-of-charge operation. *J Power Sources* 2013;231:34–38. doi:10.1016/j.jpowsour.2012.12.083.
- [30] A Kirchev, L Serra, S Dumenil, G Brichard, M Alias, B Jammet, et al. Carbon honeycomb grids for advanced lead-acid batteries. Part III: technology scale-up. *J Power Sources* 2015;299. doi:10.1016/j.jpowsour.2015.09.010.
- [31] LA Yolshina, VA Yolshina, AN Yolshin, SV Plaksin. Novel lead-graphene and lead-graphite metallic composite materials for possible applications as positive electrode grid in lead-acid battery. *J Power Sources* 2015;278:87–97. doi:10.1016/j.jpowsour.2014.12.036.
- [32] M Chen, L Wang, H Yang, S Zhao, H Xu, G Wu. Nanocarbon/oxide composite catalysts for bifunctional oxygen reduction and evolution in reversible alkaline fuel cells: a mini review. *J Power Sources* 2017. doi:10.1016/j.jpowsour.2017.08.062.
- [33] K Dhanabalan, T Sadhasivam, SC Kim, JJ Eun, J Shim, D Jeon, et al. Novel core-shell structure of a lead-activated carbon (Pb@AC) for advanced lead-acid battery systems. *J Mater Sci Mater Electron* 2017;28:10349–10356. doi:10.1007/s10854-017-6804-y.
- [34] L Wang, H Zhang, W Zhang, H Guo, G Cao, H Zhao, et al. A new nano lead-doped mesoporous carbon composite as negative electrode additives for ultralong-cyclability lead-carbon batteries. *Chem Eng J* 2018;337:201–209. doi:10.1016/j.cej.2017.12.089.
- [35] L Wang, W Zhang, L Gu, Y Gong, G Cao, H Zhao, et al. Tracking the morphology evolution of nano-lead electrodeposits on the internal surface of porous carbon and its influence on lead-carbon batteries. *Electrochim Acta* 2016;222:376–384. doi:10.1016/j.electacta.2016.10.189.
- [36] L Wang, H Zhang, W Zhang, G Cao, H Zhao, Y Yang. Enhancing cycle performance of lead-carbon battery anodes by lead-doped porous carbon composite and graphite additives. *Mater Lett* 2017;206:113–116. doi:10.1016/j.matlet.2017.06.120.
- [37] J Chmiola, G Yushin, Y Gogotsi, C Portet, P Simon, PL Taberna. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. *Science* 2006;313:1760–1763.
- [38] Y Li, Z Li, PK Shen. Simultaneous formation of ultrahigh surface area and three-dimensional hierarchical porous graphene-like networks for fast and highly stable supercapacitors. *Adv Mater* 2013;25:2474–2480. doi:10.1002/adma.201205332.
- [39] ZS Wu, Y Sun, YZ Tan, S Yang, X Feng, K Müllen. Three-dimensional graphene-based macro- and mesoporous frameworks for high-performance electrochemical capacitive energy storage. *J Am Chem Soc* 2012;134. doi:10.1021/ja308676h. 19532–5.
- [40] WL Zhang, J Yin, ZQ Lin, J Shi, C Wang, DB Liu, et al. Lead-carbon electrode designed for renewable energy storage with superior performance in partial state of charge operation. *J Power Sources* 2017;342:183–191. doi:10.1016/j.jpowsour.2016.12.061.
- [41] D Pavlov, T Rogachev, P Nikolov, G Petkova. Mechanism of action of electrochemically active carbons on the processes that take place at the negative plates of lead-acid batteries. *J Power Sources* 2009;191:58–75. doi:10.1016/j.jpowsour.2008.11.056.
- [42] D Liu, W Zhang, H Lin, Y Li, H Lu, Y Wang. A green technology for the preparation of high capacitance rice husk-based activated carbon. *J Clean Prod* 2016;112:1190–1198. doi:10.1016/j.jclepro.2015.07.005.
- [43] J Yin, N Lin, Z-Q Lin, Y Wang, J Shi, J-P Bao, et al. Towards renewable energy storage: understanding the roles of rice husk-based hierarchical porous carbon in the negative electrode of lead-carbon battery. *J Energy Storage* 2019;24:100756. doi:10.1016/j.jest.2019.100756.
- [44] MM Kashani-Motlagh, MK Mahmoudabad. Synthesis and characterization of lead oxide nano-powders by sol-gel method. *J Sol Gel Sci Technol* 2011;59:106–1

- [53] T Huang, W Ou, B Feng, B Huang, M Liu, W Zhao, et al. Researches on current distribution and plate conductivity of valve-regulated lead-acid batteries. *J Power Sources* 2012;210:7–14. doi:10.1016/j.jpowsour.2012.02.086.
- [54] M Calábek, K Míčka, P Bača, P Křivák. Influence of grid design on current distribution over the electrode surface in a lead-acid cell. *J Power Sources* 2000;85:145–148. doi:10.1016/S0378-7753(99)00393-6.
- [55] D Schulte, T Sanders, W Waag, J Kowal, DU Sauer, E Karden. Automatic device for continuous measurement of potential distribution and acid stratification in flooded lead-acid batteries. *J Power Sources* 2013;221:114–121. doi:10.1016/j.jpowsour.2012.07.072.
- [56] D Nakhaie, PH Benhangi, A Alfantazi, A Davoodi. The effect of grid configurations on potential and current density distributions in positive plate of lead-acid battery via numerical modeling. *Electrochim Acta* 2014;115:189–196. doi:10.1016/j.electacta.2013.10.152.
- [57] B Hong, L Jiang, H Xue, F Liu, M Jia, J Li, et al. Characterization of nano-lead-doped active carbon and its application in lead-acid battery. *J Power Sources* 2014;270:332–341. doi:10.1016/j.jpowsour.2014.07.145.
- [58] M Saravanan, P Sennu, M Ganesan, S Ambalavanan. Multi-walled carbon nanotubes percolation network enhanced the performance of negative electrode for lead-acid battery. *J Electrochem Soc* 2013;160:A70–A76. doi:10.1149/2.062301jes.
- [59] P Tundorn, O Chailapakul, N Tantavichet. Polyaspartate as a gelled electrolyte additive to improve the performance of the gel valve-regulated lead-acid batteries under 100 % depth of discharge and partial-state-of charge conditions. *J Solid State Electrochem* 2016;20:801–811. doi:10.1007/s10008-015-3117-z.
- [60] H Wang, Z Liu, Q Liang, H Zhong, GC Han, S Zhang, et al. A facile method for preparation of doped-N carbon material based on sisal and application for lead-carbon battery. *J Clean Prod* 2018;197:332–338. doi:10.1016/j.jclepro.2018.06.214.