Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Informarion

The effect of barium sulfate doped lead oxide as positive active materials on the performance of lead acid battery

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Supplementary Methods

The measurement procedure of barium sulfate

0.2 g sample was weighed in a small beaker, 15 mL aqua regia was added into the beaker, and the mixture was boiled until the solid became white, then the solution was filtered with 0.45 micron filter paper to a constant, and extra water was added to volume of 50 mL. The content of barium ion in the solution was measured by ICP (Perkin Elmer Optima 8300, American). We had compared the method by XRF and ICP, the results implied that the method of ICP-OES is more accurate in agreement with the literature [1].

[1] D. Sanchez-Rodas, A. M. de la Campa and L. Alsioufi, Anal Chim Acta, 2015, 898, 1-18.

The preparation procedure for the working electrode

First, lead oxide was mixed with carbon black and PVDF were mixed according to the mass ratio of 9:1:1 in the mortar, followed by grinding using pestle and mortar for about 30 minutes to prepare a homogeneous slurry. After initial mixing, NMP was added to the mixture and the mixture was ground further until the mixture becomes viscous. Then the resulting paste was dropped onto the surface of glassy carbon electrode, followed by drying in an oven at 60 ^{o}C for 24 hours.

The measurement method for metallic lead

m gram of sample was mixed and boiled with 3 mL NH_4Ac (20% V/V) in a beaker. After washing with deionized water for 3 times, the solid was mixed with 5 mL HNO_3, 5 mL hexamethylene tetramine, and three drops of dimethyl phenol orange. Then *V* ml of EDTA (0.1 M) was added dropwise until the colour of solution became bright yellow。The content of metallic Pb can be calculated as follows：$Pb\%=0.1\times V\times 20.719/m\times 100\%$

The measurement method for lead dioxide

The sulfur content of sample was measured using frequency infrared carbon and sulfur analyzer (HCS140, Shanghai). The content of lead dioxide was calculated by subtracting the percentage of the lead sulfate, which was deduced from the sulfur content.

The detailed parameters for the battery

Self-synthesized lead oxides were used as positive active material (PAM) in the lead acid battery assembly. In order to measure the performance of the positive active mass, negative plates from a commercial source were used. Positive pastes were prepared with the components listed in Table S1.

The grids used in battery assembly are low antimony alloys of Sn-Al-Ca-Pb. The size of the plate was 35 mm×60 mm×1.2 mm. Fig. S1 shows the schematic diagram of the assembly process for making lead acid battery. After mixing and pasting, the positive plates were cured in a curing vessel at a relative humidity of 95% and a temperature of 80 ^{o}C. The cured pasted plates were dried at 70 ^{o}C for 20 h. The formation process of plates was carried out in a sulfuric acid solution with a specific gravity of 1.15 g·cm^{-3}, including two processes. In the first process, the cured plate was soaking in sulfuric acid solution on open circuit for 2 h, resulting in formation of 3BS, 1BS and small amounts of $PbSO_4$. In the second process, the formation of positive plate was carried out under a constant current for 48 h (sextuple theory capacity). A dried positive plate was coupled with two commercial negative plates made from ball-milled lead oxides soaking in sulfur acid solution (1.335 g·cm^{-3}) electrolyte so that testing batteries under 2 V/2 Ah could be made. In this study, 2 Ah testing battery was designed. The theoretical capacity of assembled battery corresponding to 27.5 g novel lead oxide as active material is 2.0 Ah.

Supplementary Tables and Figures

Table S1The components of positive paste for the battery assembly

No.	Compound	Wt%
1	Lead oxide powder	80.31
2	Sulfur acid (d=1.4)	8.83
3	Distilled water	10.84
4	Fibers	0.01

Table S2 Chemical compositions of spent lead acid battery paste

Compents	$PbSO_4$	PbO_2	PbO	Metallic Pb
Percentage (wt %)	65	30	4.5	0.5

Table S3 Physicochemical characteristics of the novel lead oxide compared to traditional ball-milled lead oxide.

Types of lead oxide	Apparent Density /g·cm^{-3}	Oxidizability /%	Water-absorption value /ml·kg^{-1}	Acid-absorption value /g·kg^{-1}
synthesized lead oxide	1.81	79.6	246.0	448.0
Traditional balling lead oxide [a]	1.93	83.2	110.0	381.3

[a] Note: The traditional ball-milled lead oxide was provided by Wuhan Changguang Power Sources. Co. Ltd

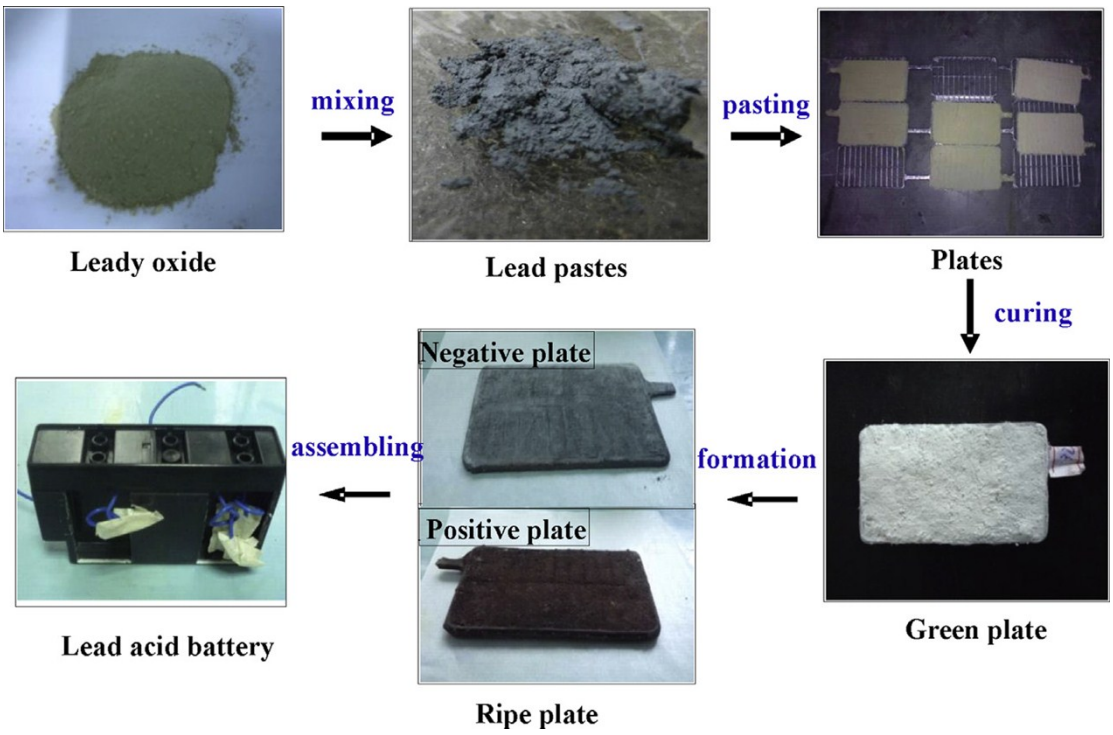

Fig. S1 Schematic diagram of the assembly of lead acid battery

Reference from our previous research:

D. Yang, J. Liu, Q. Wang, X. Yuan, X. Zhu, L. Li, W. Zhang, Y. Hu, X. Sun, R.V. Kumar, Journal of Power Sources, 257 (2014) 27-36.

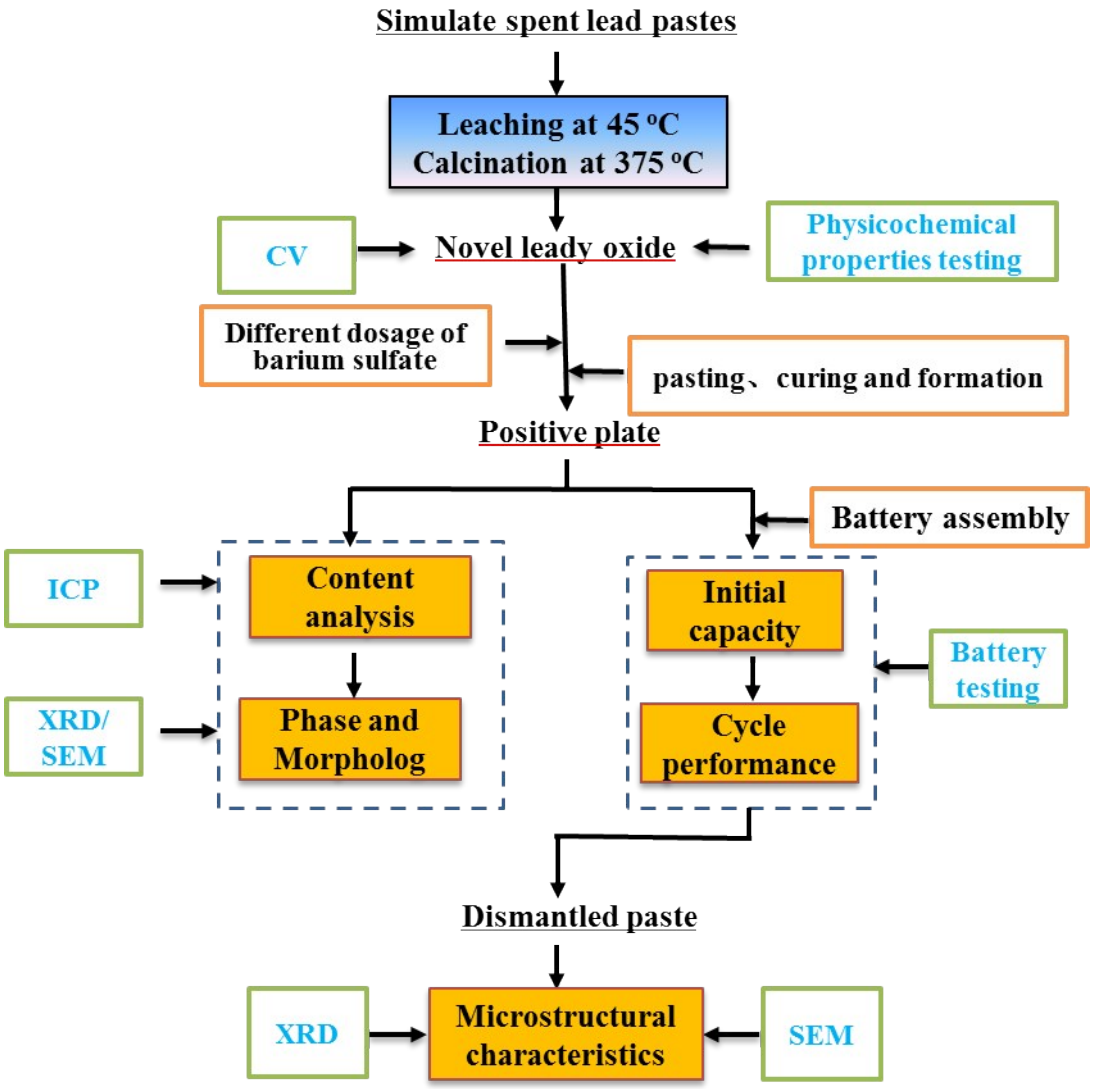

Fig S2 The flow sheet of experiments.

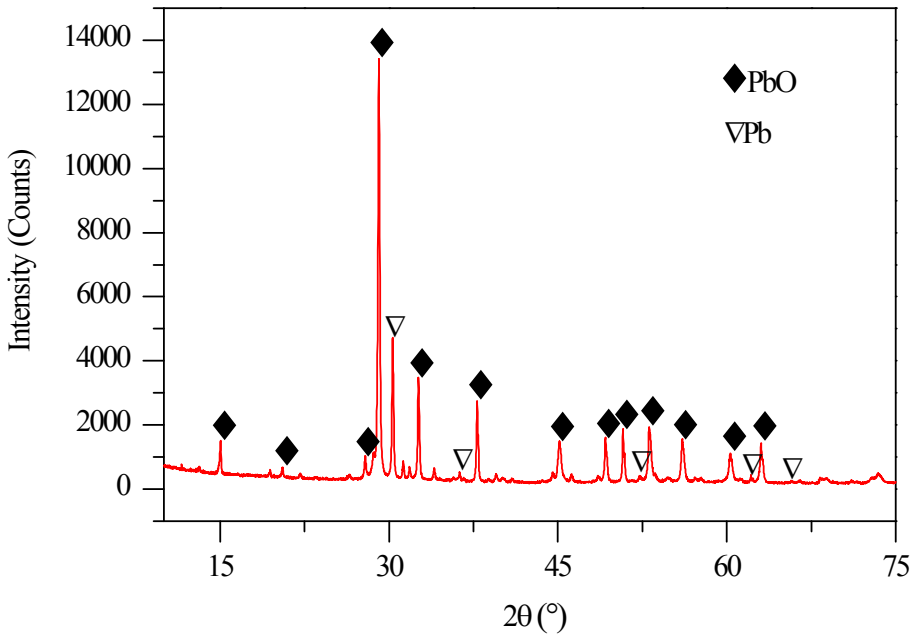

Fig S3 The XRD pattern of the lead oxide.

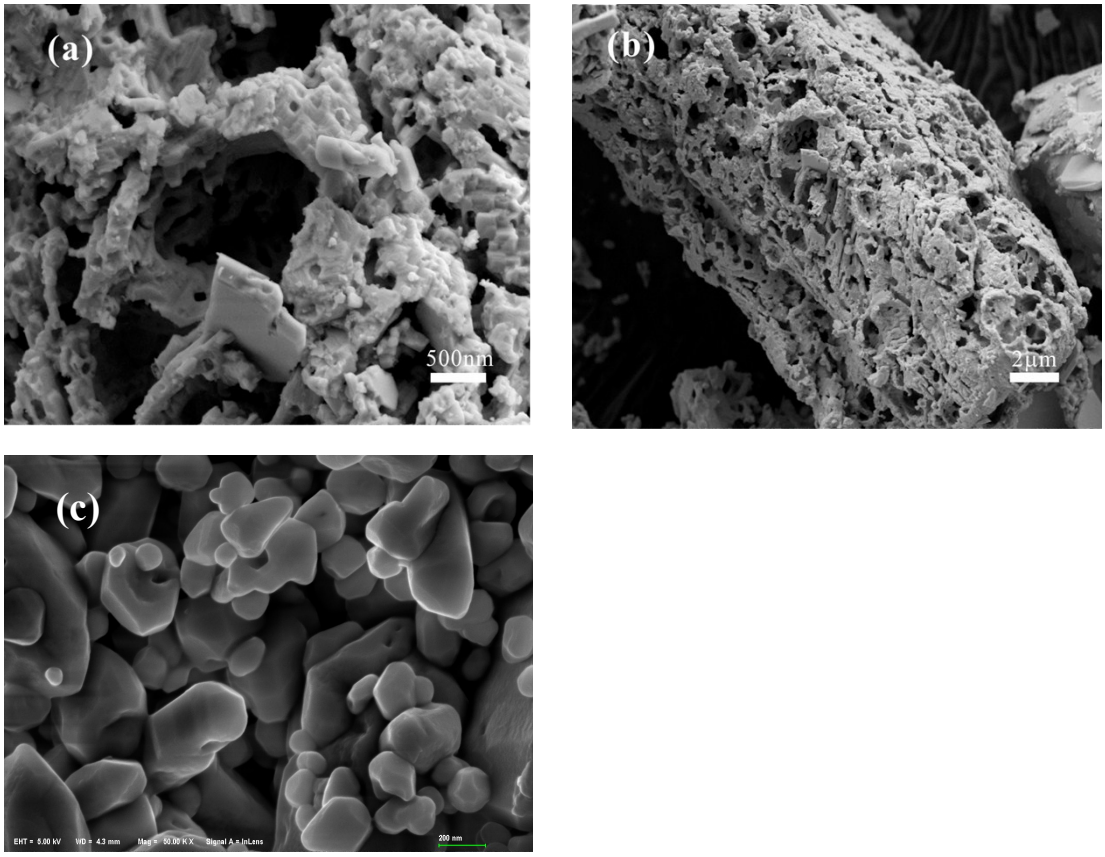

Fig S4 The SEM images of (a-b) the lead oxide, (c) barium sulfate.

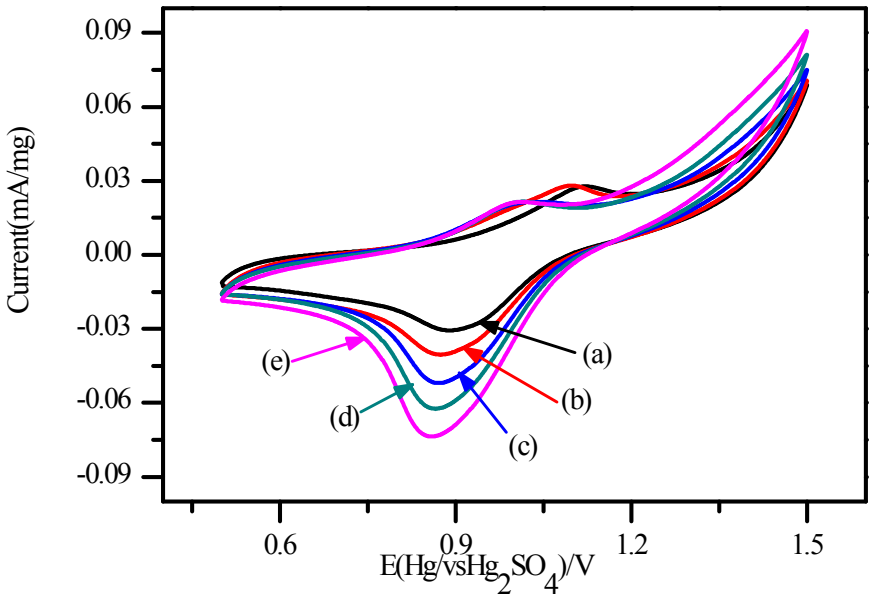

Fig S5 CV curves of lead oxide: with different cycles.
(a) 5th cycle, (b) 10th cycle, (c) 15th cycle, (d) 20th cycle and (e) 30th cycle.