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Comment on "Environmentally responsible fabrication of efficient perovskite solar cells from recycled car batteries" by Po-Yen Chen, Jifa Qi, Matthew T. Klug, Xiangnan Dang, Paula T. Hammond and Angela M. Belcher, *Energy Environ. Sci.*, 2014

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A paper published in *Energy and Environmental Science* by Po-Yen Chen *et al*. reported on a new route for fabricating perovskite solar cells using "recycled car batteries" (spent lead acid batteries) as starting materials. Multiple lines of evidence show that it was a new lead acid battery and not a recycled one that was used to synthesize lead iodide perovskite materials in this paper. As the components of electrodes are different between new batteries and spent ones, this fabricating method would not be applicable for use in recycled car batteries.

In a recent paper, Po-Yen Chen *et al.* reported on the fabrication of organic lead halide perovskite solar cells though recycling spent lead acid batteries. Generally, the pastes that are scraped from spent lead acid battery electrodes contain $PbSO_4$ (50-60%), PbO_2 (30-35%), PbO (4-10%) and Pb (1-5%) [1-4], while the lead material derived from cathodes and anodes of batteries in this study were pure PbO_2 (＞97%) and Pb (＞99.9%), respectively. This suggests that the starting experimental object was not a spent battery but, rather, a new one.

In the manufacture of a lead acid battery, lead oxides, the active materials of electrodes, undergo mixing, pasting, curing and formation process [5-7]. After all these procedures the lead oxides that containing 70-80% PbO and 20-30% Pb are finally transformed into PbO_2 and Pb. A schematic diagram of the assembly process used in making a lead acid battery is illustrated in Fig. 1, and variations in the lead-containing components are also described. Specifically in formation process, under a constant current for appropriate time, lead sulfates (mainly $4PbO{\cdot}PbSO_4$, $3PbO{\cdot}PbSO_4{\cdot}H_2O$ and $PbO{\cdot}PbSO_4$) on the positive plate are converted into PbO_2, while lead sulfates on the negative plate are transformed into elemental Pb. When a new lead acid battery is assembled, the PbO_2 content in the cathode and the Pb content in the anode, respectively, account for above 80% of the total lead material with a small amount of $PbSO_4$ [5]. This is consistent with the content of PbO_2 and Pb that was removed from the battery in Po-Yen Chen´s paper (shown in Fig. 1, Fig. S1a and S1b in Po-Yen Chen´s paper).

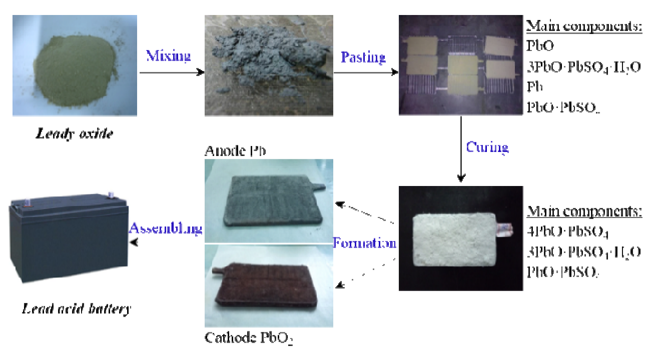


Fig. 1 Schematic diagram of the assembly process for making a lead acid battery [5, 6]

During the discharging and charging of a lead acid battery, the active materials of electrodes undergo repeated oxidation and reduction reactions [8], as shown in Eqs. (1) - (4):

Discharge process:

$$PbO_2 + H_2SO_4 + 2H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O \quad (1)$$

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \quad (2)$$

Charge process:

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e^- \quad (3)$$

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \quad (4)$$

After several cycles, lead sulfate crystals become so thick and large bigger that it becomes impossible to convert them into PbO_2 and Pb, a process that is referred to as irreversible sulfation. When the irreversible lead sulfate content reaches a critical level, the lead acid battery can no longer be charged anymore. Therefore, lead sulfate which generally accounts for ＞50% of the total lead material, is the major constituent in spent lead acid battery pastes.

The evidence mentioned above proves that the car battery that was disassembled in this study was, in fact, a new lead acid battery. This discrepancy indicates that the "fabrication of efficient perovskite solar cells from recycled car batteries" described in that report is erroneous. Moreover, if paste from a spent lead acid battery were used as starting materials to synthesize lead iodide perovskite materials according to the given process (shown in Fig. 1 in Po-Yen Chen´s paper), most of the $PbSO_4$ would remain in the solid residues without recycling. Meanwhile, high purity Pb^{2+} cannot be obtained because of the solubility of $PbSO_4$ in nitric acid (6.7 mmol/L in 1 mol/L nitric acid) [9], which may affect the purity of lead iodide perovskite materials and further influence the electrochemical performance of perovskite solar cells.

Concerning the reuse of $PbSO_4$ in spent batteries, X. J. Sun *et al.* [10] recently demonstrated a pathway for the synthesis of $Pb(CH_3COO)_2{\cdot}3H_2O$ from spent lead acid battery pastes by applying a desulphurization and leaching process. Based on the research of Po-Yen Chen and X. J. Sun, an improved method for the synthesis of lead iodide perovskite is proposed and shown in Fig. 2. The main reactions between the lead compounds and reagents are presented in the following Equations (5) - (8):

Desulphurization process:

$$PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3 + (NH_4)_2SO_4 \quad (5)$$

Leaching process:

$$PbCO_3 + 2CH_3COOH \rightarrow Pb(CH_3COO)_2 + CO_2\uparrow + H_2O \quad (6)$$

$$PbO_2 + 2CH_3COOH + H_2O_2 \rightarrow Pb(CH_3COO)_2 + 2H_2O + O_2\uparrow \quad (7)$$

$$PbO + 2CH_3COOH \rightarrow Pb(CH_3COO)_2 + 2H_2O \quad (8)$$

After the desulphurizing and leaching process, the recycling product from spent lead acid battery, a $Pb(CH_3COO)_2$ solution, can act as the precursor in generating PbI_2 and the further manufacture of lead iodide perovskite materials for perovskite solar cells.

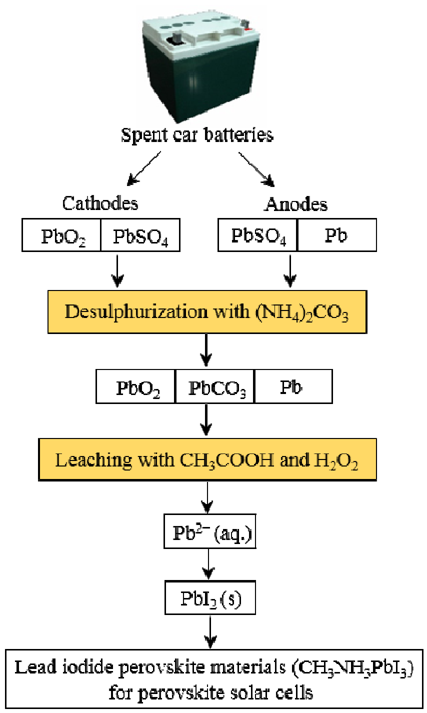
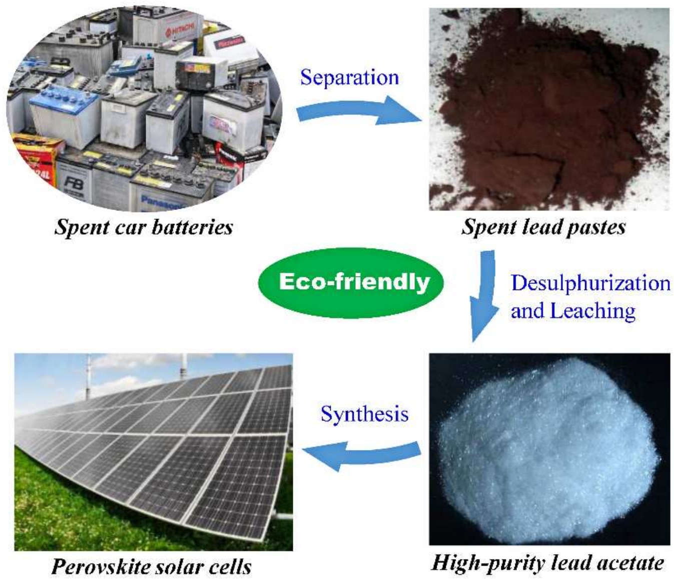


Fig. 2 Schematic illustration of an improved method for the synthesis of lead iodide perovskite materials from spent car batteries

References

1. N. K. Lyakov, D. A. Atanasova, V. S. Vassilev and G. A. Haralampiev, *J. Power Sources*, 2007, **171**, 960-965.
2. M. S. Sonmez and R. V. Kumar, *Hydrometallurgy*, 2009, **95**, 82-86.
3. L. Li, X. Zhu, D. Yang, L. Gao, J. Liu, R. V. Kumar and J. Yang, *J. Hazard. Mater.*, 2012, **203**, 274-282.
4. X. Zhu, L. Li, X. Sun, D. Yang, L. Gao, J. Liu, R. V. Kumar and J. Yang, *Hydrometallurgy*, 2012, **117**, 24-31.
5. D. Pavlov, in *Lead-Acid Batteries: Science and Technology*, ed. D. Pavlov, Elsevier, Amsterdam, 2011, pp. 363-499.
6. D. Yang, J. Liu, Q. Wang, X. Yuan, X. Zhu, L. Li, W. Zhang, Y. Hu, X. Sun, R. V. Kumar and J. Yang, *J. Power Sources*, 2014, **257**, 27-36.
7. M. Sorge, T. Bean, T. Woodland, J. Canning, I. F. Cheng and D. B. Edwards, *J. Power Sources*, 2014, **266**, 496-511.
8. J. E. Manders, L. T. Lam, K. Peters, R. D. Prengaman and E. M. Valeriote, *J. Power Sources*, 1996, **59**, 199-207.
9. H. H. Willard and J. L. Kassner, *J. Am. Chem. Soc.*, 1930, **52**, 2402-2408.
10. X. Sun, J. Yang, W. Zhang, X. Zhu, Y. Hu, D. Yang, X. Yuan, W. Yu, J. Dong, H. Wang, L. Li, R. V. Kumar and S. Liang, *J. Power Sources*, 2014, **269**, 565-576.



The use of components of spent car batteries, rather than new ones, to produce peroviskite solar cells constitutes an eco-friendly process.