Supplementary Information

Enhanced Cycle Life of Lead-acid Battery Using Graphene as a Sulfation Suppression Additive in Negative Active Material

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The Gr used in this research was all synthesized by the CVD method according to the growth profile as shown in Fig. S1. Gr powders can be obtained from freestanding 3D Gr, which are composed of heterogeneous layer numbers with single-, few-, and multi-layer Gr. The synthesized Gr possesses lattice grain structures with domain in micron scale. The charge transport along the Gr sheets is greatly affected by Gr grain size and number of defects.^{S1} Increasing the domain size essentially reduces the number of defects on the Gr sheets with an improvement in charge transport. The synthesized Gr possesses lattice grain structures with large domain size that are commensurate to nickel foam lattice are shown in Fig. S2a and Fig. S2b. The lattice grain structures remain, even after etching of nickel substrates and ranged from a few

to tens of microns as shown in Fig. S2c and Fig. S2d. The electron transport along the Gr sheets is greatly affected by Gr grain size and number of defects.^{S1} Grain boundaries are formed as a result of Gr domains coalescence that contain defects and affect the Gr electronic properties.^{S2} Increasing the domain size essentially reduces the number of defects on the Gr sheets with an improvement in electron transport. The SEM image shows in Fig. S2c illustrates that our CVD-synthesized Gr contains a combination of single-, few-, and multi-layered Gr from different shades of Gr domains on the magnified image as reported previously.^{S3} As proposed by Li et al.,^{S4, S5} the growing mechanism of 3D Gr on nickel foam involves surface adsorption of carbon atoms at elevated temperatures, followed by Gr layer formation via out-diffusion onto the nickel surface during the rapid cooling stage. Upon transforming from 3D Gr foam to 3D Gr framents, Gr remains as interconnected three-dimensional structure as shown in Fig. S2e and Fig. S2f.

The Raman spectra shown in Fig. S3 demonstrates the high quality of CVD-synthesized Gr is defect-free with the G peak at ~1580 cm⁻¹ and the 2D peak at ~2700 cm⁻¹ confirming the presence of graphitic carbon. The absence of the D peak, which is typically at ~1350 cm⁻¹, indicates that a high quality of Gr has been achieved. While the positions of G and 2D peaks remain unchanged after processing into powder form as shown in Fig. S3.

TEM results, as shown in Fig. S4, further confirm the existence of different Gr layers. TEM images taken along the Gr folding edges in Fig. S4a and Fig. S4b demonstrate few-layered and multi-layered Gr structures respectively. SEM images with morphologies of other carbon additives, such as carbon fiber, carbon black and multi-walled carbon nanotube, are shown in Fig S5. PSoC results of Pb and PbG with various Gr wt% are shown in Fig. S6. PbG plates with 0.2 wt% showed the best performance with over 140% enhancement based on the average cycle number. We speculated that due to high aspect ratio and low density of Gr, an optimum percentage of carbon additives is required to maintain a balance between enhanced conductive pathway and hydrogen gas evolution. It is reported that significant hydrogen evolution due to addition of carbon additives during the charging step brings negative impact to the battery cycling performance. ^{S6, S7} Studies of various percentage effect and more runs of PSoC cycle test are in progress and will be included in future publication.

References

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Fig. S1 Growth profile for chemical vapor deposition of 3D Gr.



Fig. S2. Optical microscopy images of (a) nickel foam surface and (b) CVD synthesized Gr on nickel foam surface. SEM images of (c) and (d) magnified view of freestanding Gr foam surface and (e) and (f) Gr powder.



Fig. S3. Raman spectrum of CVD-synthesized 3D Gr and Gr powder.



Fig. S4. TEM images of CVD synthesized Gr showing (a) few-layered and (b) multi-layered structures. Inset pictures are their corresponding folding positions where the magnified images were taken.



Fig S5 SEM images of other carbon additives (a) and (b) carbon fiber, (c) carbon black and (d) multi-walled carbon nanotube.



Fig. S6 (a) PSoC results of one run and (b) average PSoC cycle number of Pb and PbG plates at various Gr wt%.