

Electronic Supplementary Information

Nanosized LiFePO_4 -decorated carbon foam for 3D micro batteries: A study of structure and electrochemical performance

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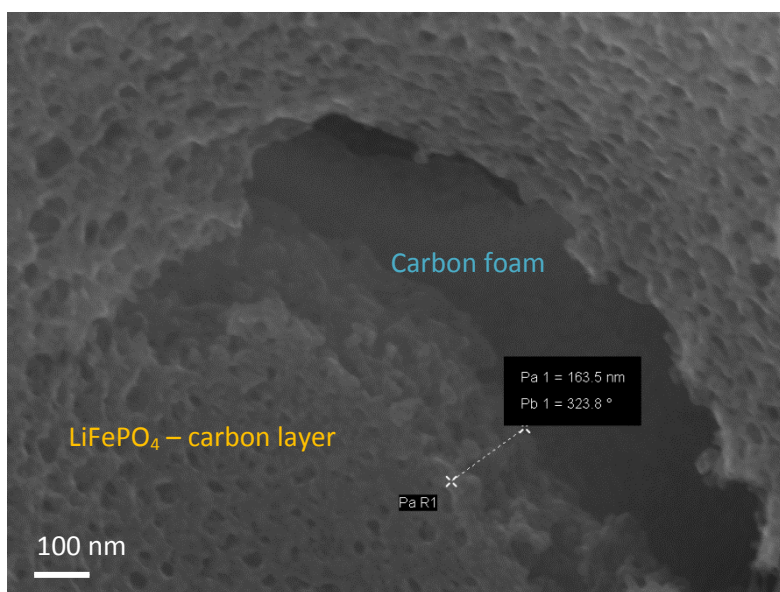


Figure S1: SEM image showing the thickness of LiFePO₄ coating on the top of a carbon foam electrode.

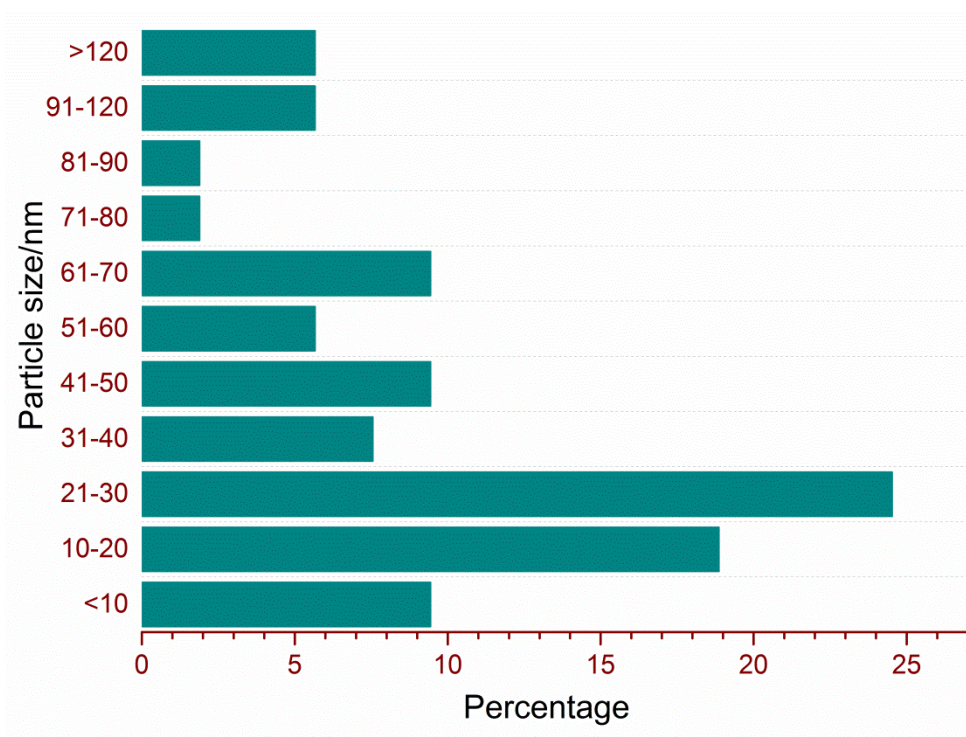


Figure S2: Particle size distribution evaluated from TEM and SEM data displays the majority of the LiFePO₄ nanoparticles are below 70 nm.

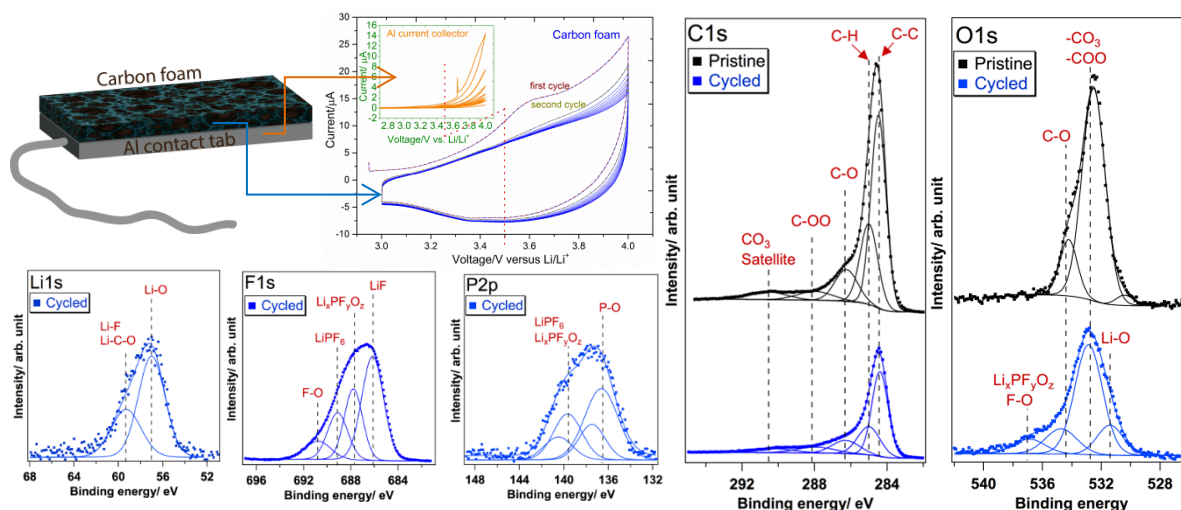


Figure S3: Cyclic voltammograms of polyHIPE-derived carbon foam cycled against lithium at a scan rate of 0.05 mV/s in the voltage range of 3.0-4.0 V. (a) An abrupt rise in oxidation current in the first cycle hints at the onset of parasitic reactions. Inset displays CVs for the corrosion of aluminum tab used as a contact beneath the carbon foam. XPS spectra acquired for the pristine and cycled carbon foams: spectra of the cycled carbon indicate the decomposition of the electrolyte salt.

Substrate characterization:

Prior to investigating the use of the carbon foam as a support for the cathode, it is appropriate to check the effect of sustained cycling on the surface and structure of the carbon substrate in the relevant voltage range. Thin pieces of the pristine carbon foams are cycled voltammetrically and galvanostatically in the voltage range from 3.0 to 4.0 V vs. Since the carbon foam has such a large surface area available for interfacial charge storage, there is always a background contribution due to double layer charging in. In addition to the capacitive contributions, there may be another contribution from electrolyte decomposition especially in the presence of traces of moisture or other impurities. As depicted in Figure S3, the initial cycle exhibits a rise in the oxidation current as the voltage is swept above 3.5 V versus Li/Li⁺, which is indicative of the onset of parasitic reactions occurring on the carbon electrode and, naturally, the aluminum contact underneath (inset image).¹⁻³ Clearly, the resultant background contribution decreases gradually in the subsequent cycles implying that the undesirable reactions have ceased to occur and the electrode surface is passivated. Then, the only background contribution is attributed to interfacial double layer charging. Similar behavior is seen in Figure S4 in which the carbon foam, when cycled versus Li, exhibits poor coulombic efficiency and cyclability for several cycles. To determine the origin of this parasitic current, XPS analyses were carried out on both the pristine and cycled carbon foams, as displayed in Figure S4. Most importantly, the XPS results for the cycled carbon show the presence of F, P, and Li on the surface. Both F1s and P2p spectra reveal that LiPF₆ salt has decomposed on the surface of the carbon foam and consequently formed LiF, Li_xPF_yO_z, P-O, and Li-O compounds. This verifies the decomposition of the electrolyte, in good agreement with other works.

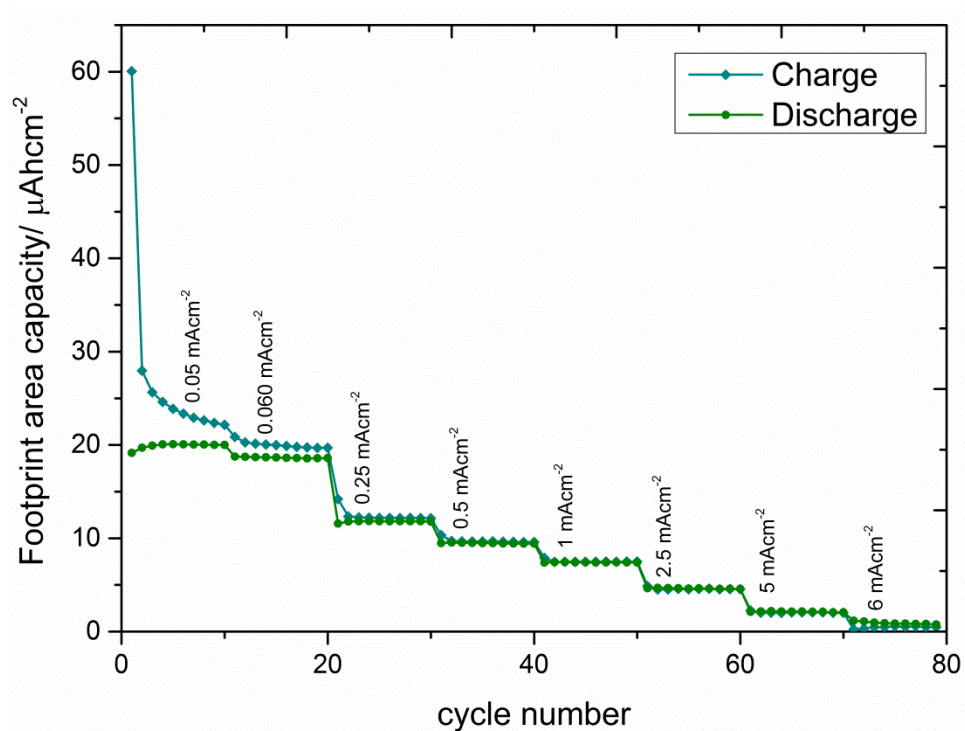


Figure S4: Background test: Pristine and freestanding carbon foam is cycled in the voltage range of 2.8 to 4.0 V vs. lithium. It can be noted that the coulombic efficiency is low for few cycles due to irreversible parasitic reactions involving the electrolyte as elucidated by XPS analyses. The contribution of the carbon to the overall capacity is insignificant. The slow rate capacity, at $\sim 0.1 \text{ mAcm}^{-2}$, is around $\sim 1.2 \%$ of the total capacity of the composite cathode.

Table 1: The table below presents a comparison of capacities of electrodes used as cathodes in microbatteries.

Material	Electrode architecture	Coating method	Footprint area capacity/ mAhcm ⁻²	Rate/ mAcm ⁻²	References
LiFePO₄	3D, polyHIPE-derived carbon foam	Sol-gel	1.72	0.1	Our electrode
LiFePO₄	3D, polyHIPE-derived carbon foam	Sol-gel	1.65	0.2 ~ 0.11 C	Our electrode
CuS-coated LiFePO₄	3D, μ -channeled silicon substrate	Electrophoretic deposition	2.1	0.1	4
LiFePO₄	3D, virus-templated metal nano-arrays	RF magnetron sputtering	0.176	0.1 C	5
LiFePO₄	3D, reticulated vitreous carbon foam	Dip-spin coating	1.5	0.25 C	6
LiCoO₂	3D, Al nano-arrays	Spray-coating, sol-gel	0.12	0.2 C	7
CuS	3D, μ -channeled silicon substrate	Electrodeposition	1.015	0.12	8
Polyaniline	3D, polyHIPE-derived carbon foam	Electrodeposition	0.46	0.1 C	9
LiCoO₂	Thin film	Screen printing	0.164	0.02	10
LiFePO₄	Thin film	RF magnetron sputtering	0.0224	0.01	11

Note: Rate is given in terms of mAcm⁻² except for those indicated by C, where C-rate is used instead.

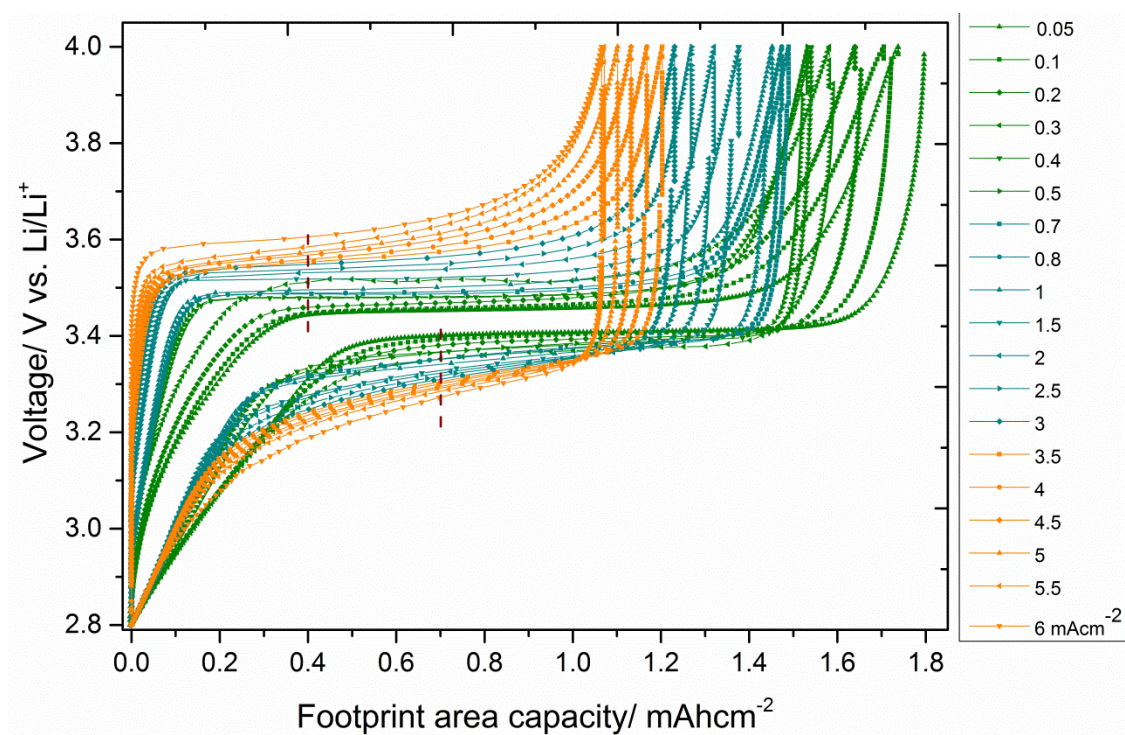


Figure S5: Voltage profiles at different current rates: Redox potentials shift increasingly along with increasing current densities partly due to ohmic losses in the porous electrode.

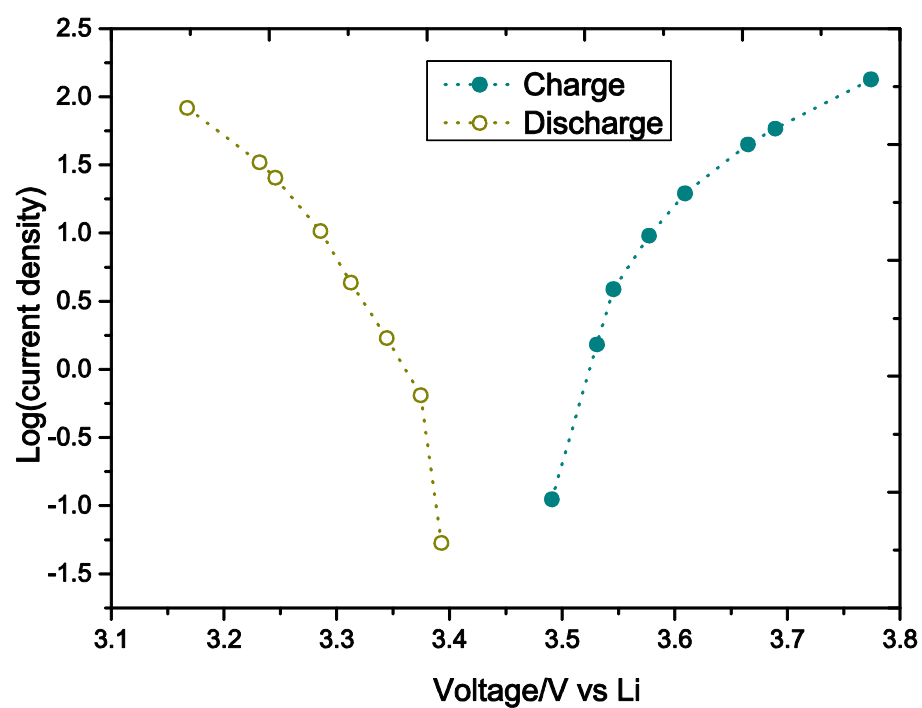


Figure S6: Logarithmic plots of charge and discharge current densities versus peak potentials are shown in this figure.

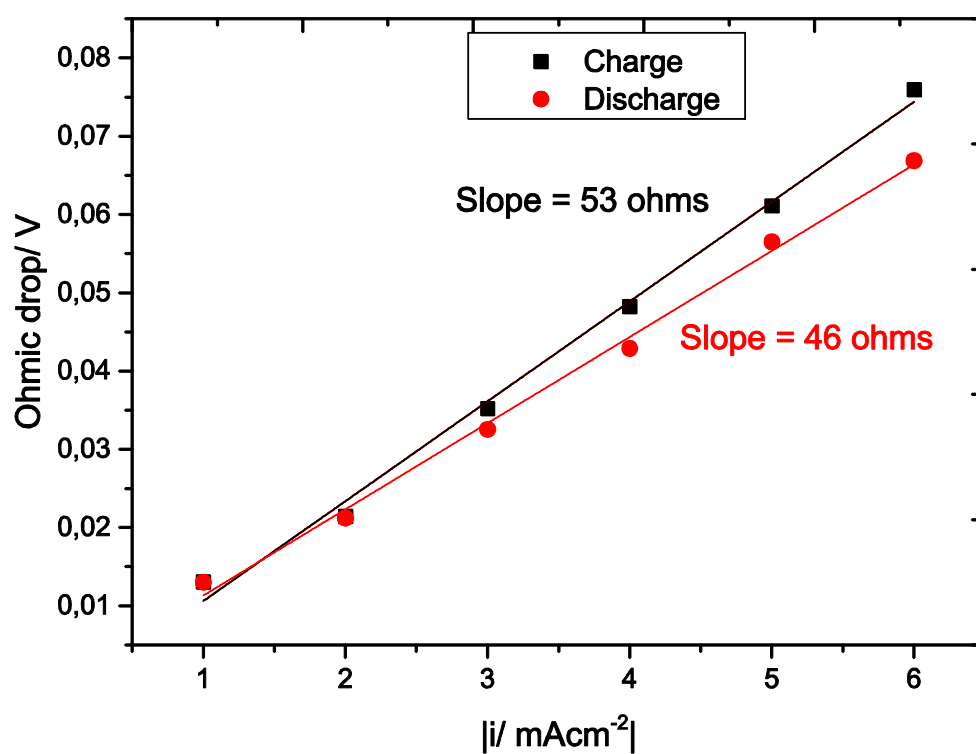


Figure S7: Plots of IR drop versus current density are shown for charge and discharge.

References

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