

Rejuvenation of Aged Graphite Anodes from Spent Lithium-Ion Batteries via a Facile Surface Treatment Strategy

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Experimental section:

Chemical Reagents: dimethyl carbonate (DMC), anhydrous methanol, and N-methyl-2-pyrrolidone (NMP) were procured from Sigma-Aldrich.

Preparation of Aged 18650-Type Cylindrical LiFePO₄ (LFP)/Graphite cell: the 18650-type cells were subjected to a cycling process within a current of 3 A (2 C-rate) and a voltage window from 2.5 V to 4.0 V until 25% of their capacities remained. To ensure maximum discharge, the cells were brought down to a voltage of 2.0 V at a current of 0.15 A and continued to discharge at 2.0 V until the current dipped below 0.075 A.

Preparation of Aged Graphite: the fully discharged 18650-type cells were carefully disassembled within a glove box. The disassembled graphite anode was reshaped into Φ 12 cm round electrodes for further processing. The reshaped electrodes, which were coated on both sides, were thoroughly washed three times with dimethyl carbonate (DMC) to remove the electrolyte. Following the cleaning, they were dried in the transfer chamber of the glove box under vacuum conditions.

Rejuvenation of Graphite Electrode: A portion of the aged graphite were taken out of the glove box, immersed in 0.1 M formic acid for 60 minutes. After being washed three times with deionized water by a gentle soaking process, the electrode, now referred to as Rejuvenated Graphite, were dried in a vacuum oven at 80 °C for 12 h.

Characterization: The electrodes underwent a series of characterizations using various techniques. Field emission scanning electron microscope (FESEM) analysis was carried out on a JEOL JSM 7600F SEM. Transmission electron microscope (TEM) analysis was performed on a FEI Titan monochromatic scanning TEM operating at 200 kV. X-ray diffraction (XRD) patterns were generated using a Bruker D8 Advance XRD equipped with Cu-K α radiation of 1.5418 Å, operated at 40 kV and 40 mA. X-Ray Photoelectron spectroscopy (XPS) measurements were carried out using a Kratos AXIS Supra+ X-Ray Photoelectron Spectrometer System (Kratos Analytical Ltd, UK) with a large 500 mm Rowland circle monochromated Al K α (1486.6 eV) X-ray source. Energy-dispersive X-ray spectroscopy (EDX) was conducted using a JEOL 7600F Field Emission Scanning Electron Microscope fitted with an Oxford energy-dispersive X-ray detector. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectra were acquired using IONTOF TOF-SIMS 5 equipment. Finally, Raman spectra were recorded via confocal Raman microscopy (Renishaw inVia Raman microscope) employing a laser at 785 nm.

Electrochemical Performance Analysis: The electrochemical properties of the electrodes were investigated using CR2032-type coin cells, each comprising a Li metal counter electrode with a diameter of 15.8 mm and a Celgard 2400 separator. The employed electrolyte was a 1.2 M LiPF₆ solution in an equal volume mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), with a total volume of 80 μ L. For the assembly of the coin cells, the working electrodes (either rejuvenated or aged graphite) were readied through the removal of one layer of coating. This process involved applying a droplet of anhydrous methanol to one side of the double-coated electrodes to strip off the coating, while the opposite side was left intact for subsequent coin cell assembly. Galvanostatic charge-discharge tests were then carried out under ambient conditions, at various currents, within a voltage range of 0 to 2.0 V, using LANDHE battery testing equipment. Furthermore, electrochemical impedance spectroscopy

(EIS) tests were conducted within a frequency range of 100 kHz to 10 mHz at open circuit voltage, using an Autolab (Metrohm PGSTAT302N) workstation.

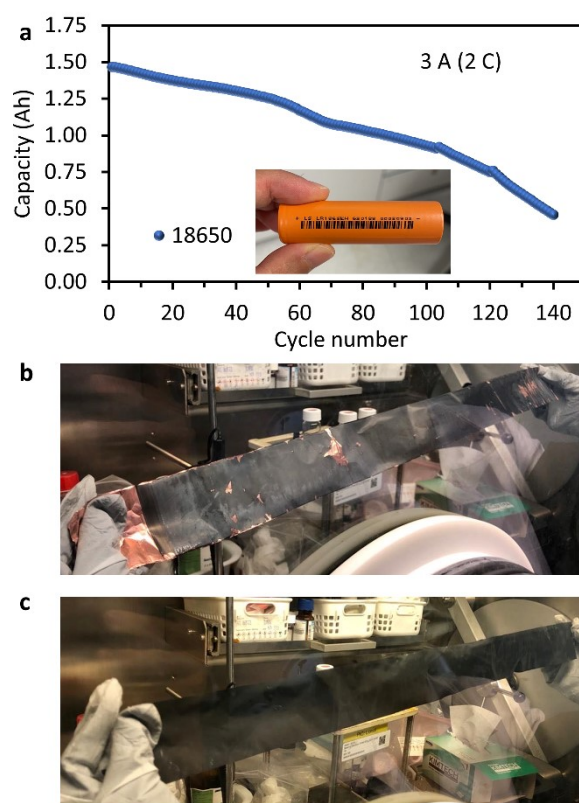


Figure S1: The cycled 18650-type cylindrical LiFePO_4 cell. (a) Cycling curve within charge & discharge current of 3 A, (inset: photo image of the cell). Photo images of Graphite anode (b) and LFP cathode (c) after cycling.

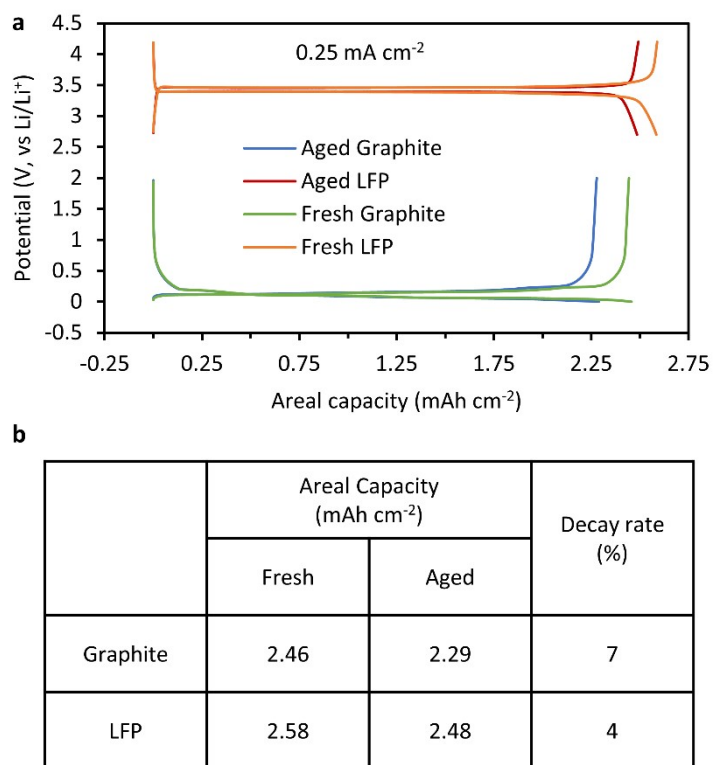


Figure S2: Areal capacity check-up (a) and decay rate calculation (b) of the aged graphite and LFP electrodes in coin-cells.

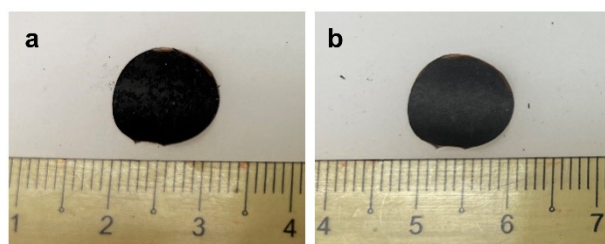


Figure S3: Photo images of (a) aged graphite and (b) rejuvenated graphite.

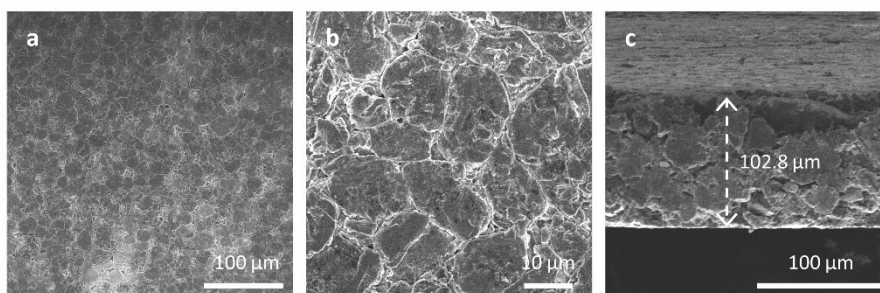


Figure S4. FESEM images of fresh graphite.

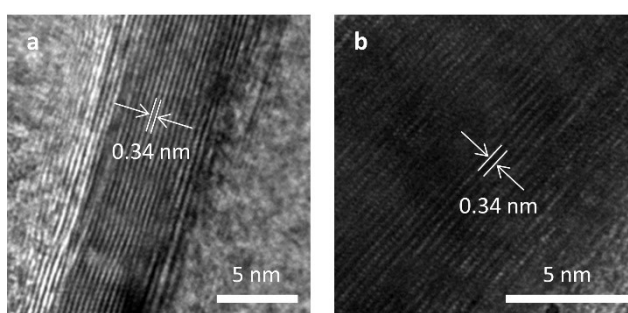


Figure S5. HRTEM images of (a) rejuvenated graphite and (b) aged graphite.

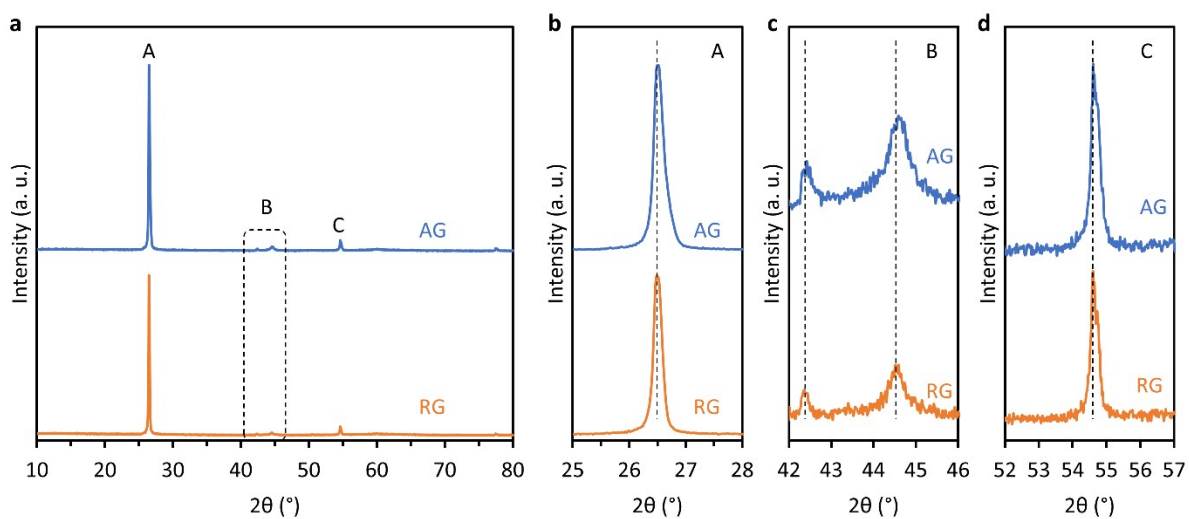


Figure S6. (a) XRD patterns of aged graphite (AG) and rejuvenated graphite (RG). (b, c, d) the enlarged patterns of the peaks A, B, C.

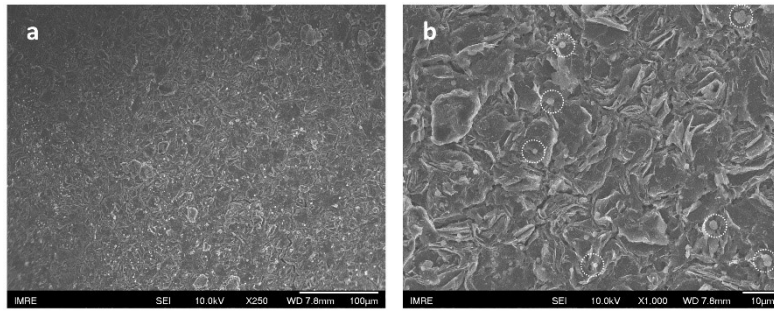


Figure S7. FESEM images of rejuvenated graphite within soaking time of 10 min.

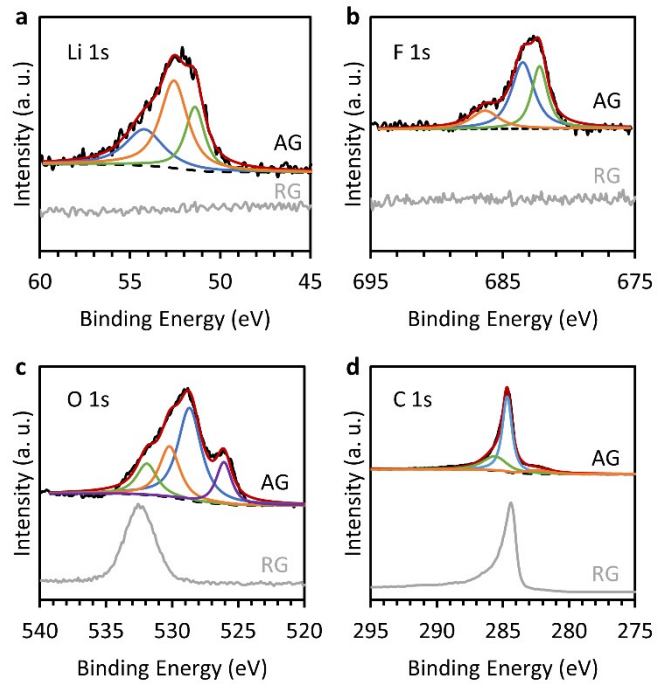


Figure S8. XPS spectra of aged graphite and rejuvenated graphite.

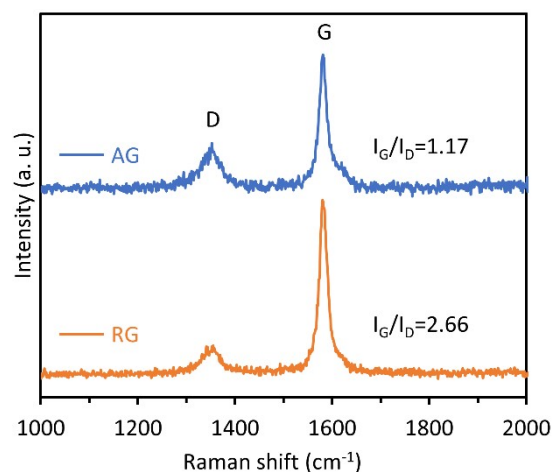


Figure S9. Raman spectra of aged graphite and rejuvenated graphite.

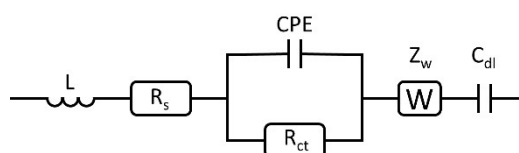


Figure S10. Equivalent circuit of EIS plots of aged graphite and rejuvenated graphite.

Table S1. Fitted results of each element of rejuvenated graphite and aged graphite.

Element	Rejuvenated graphite		Aged graphite	
	Value	Estimated Error (%)	Value	Estimated Error (%)
L	3.2403×10^{-7}	1.381	3.2655×10^{-7}	1.642
R_s	2.4874	0.433	2.3029	0.573
CPE (Y0)	1.8725×10^{-5}	2.791	2.0362×10^{-5}	2.963
CPE (N)	0.85058	0.327	0.82696	0.358
R_{ct}	40.312	0.541	59.88	0.626
W	0.0146	2.594	0.013312	2.997
C_{dl}	0.0018532	0.649	0.0030507	1.058
χ^2	0.11096		0.17312	

The possible reactions between formic acid and interfacial blocking layer are listed below:

