Supplementary Information Material for:

How Improper Use of Activated Carbon Leads to Biased Data Interpretation in Post-Li Battery Systems

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Materials and methods

1,2,4,5-Benzenetetramine tetrahydrochloride (97.0%, Fluorochem), pyridine (Fisher Scientific), methanesulfonyl chloride (99.5%, Fisher scientific), anhydrous methanol (99.9%, Alfa Aesar), lithium methoxide (98%, Sigma Aldrich), anhydrous zinc (II) chloride (98%, Alfa Aesar), anhydrous calcium chloride (98%, Sigma Aldrich), anhydrous propylene carbonate (99.7%, Sigma Aldrich), anhydrous acetonitrile (99.8%, Sigma Aldrich), anhydrous 1,2-dimethoxyethane (99.8%, Sigma Aldrich), tetraethylene glycol dimethyl ether (99%, Sigma Aldrich) and calcium bis(trifluoromethanesulfonyl)imide (99+%, Solvionic) were used as received. Active carbon, conductive carbon and polytetrafluoroethylene (PTFE) were purchased from TOB New Energy Technology Co., Ltd. (Xiamen, China). The Glass fiber separator (GF/D) was purchased from Whatman. Active carbon cloth (ACC-5092-20) was purchased from Kynol. Swagelok cells were purchased from S4R.

Assembly and testing of two-electrode coin cells

The electrochemical tests were carried out using 2025-type coin cells with 13 mm diameter active carbon fabrics (with different working-to-counter mass ratios) used as counter and pseudo-reference electrode, and glass microfibre filter as the separator. The positive electrode composition was made by hand-grinding 50 % CP active material (Ca-Zn-PTtSA or LFP) with 40 wt.% conductive carbon (Super P carbon, C-45) and 10 wt.% PTFE as a binder. The electrodes were assembled by applying the composite powder to the positive side of the coin cell case (CR 2032, AISI 316L stainless steel) and compacting with a stainless-steel disk. The typical active material loading was of about 1.5-2 mg/cm^2. At room temperature, galvanostatic charge/discharge experiments were conducted using a Neware battery testing equipment.

Assembly and testing of three-electrode cells

The electrochemical testing in three-electrode configuration was performed in Swagelok-type cells. The assembly of the three-electrode cells was performed in an Ar-filled glovebox, with a 13 mm diameter active carbon fabric used as counter, Ag wire as pseudo reference, and glass microfiber filter as the separator. The positive electrode composition was made by hand-grinding 50 % Ca-Zn-PTtSA active material with 40 wt.% conductive carbon and 10 wt.% PTFE as a binder. The electrodes were manufactured by applying the composite powder to the plunger and compacting with a stainless-steel disk. The active material loading was typically of about 1.5-2 mg/cm^2. Galvanostatic charge/discharge experiments were conducted using a VMP galvanostat/potentiostat (Bio-Logic, France), at room temperature. The water content of the electrolytes was below 20 ppm, as determined by Karl Fischer titration, Metrohm 899 Coulometer.

Synthesis of Ca-Zn-PTtSA

In a 100 ml round-bottom flask containing 50 ml pyridine, 2.48 g 1,2,4,5-benzenetetramine tetrahydrochloride (0.01 mol, 1.0 equiv.) was added and cooled to -17°C with an ice/salt bath. Then, 3.1 ml of methanesulfonyl chloride (0.04 mol, 4.0 equiv.) was added drop wise in 30 minutes. Once the addition completed, the ice-salt bath was removed, and the solution was allowed to slowly warm up to room temperature while being stirred for another 24 hours. Afterwards, an aqueous solution of 200 ml 1 M HCl was added to the reaction mixture. The resulting precipitate was filtered and washed three times with 100 ml of 1 M HCl, followed by three additional washes with 100 ml of water. The obtained light pink powder was finally dried under vacuum at 70°C. Yield: 55%.

200 mg of H_4-PTtSA (0.44 mmol, 1.0 equiv.) and 66.83 mg lithium methoxide (1.76 mmol, 4.0 equiv.) were dissolved in 10 ml of anhydrous methanol in a 20 ml vial, inside an argon-filled glove box. After stirring for 1 hour, zinc (II) chloride (0.44 mmol, 1.0 equiv.) dissolved in 1 ml anhydrous methanol was added dropwise to the reaction mixture and left to stir for another 24 hours. Afterwards, 48.80 mg calcium chloride (0.44 mmol, 1.0 equiv.) dissolved in 1 ml of anhydrous methanol, was added dropwise to the reaction medium. After stirring for another 24 hours, the reaction medium was centrifuged to separate the precipitate and a completely transparent supernatant. The precipitate was washed three times with anhydrous methanol and three times with anhydrous ether. The resulting powder was dried in vacuum at 180°C for 14 hours. The yield was around 90%.

Preparation of self-standing activated carbon electrodes

In a mortar, 450 mg of activated carbon was mixed with 50 mg of PTFE nanoparticles and 5 mL of isopropanol. The resulting dense paste was rolled out between two sheets of weighing paper, and 13 mm diameter disks were cut from it. The self-standing electrodes were then dried overnight at 150 °C in a vacuum oven.

N_2 sorption isotherms

N_2 sorption isotherms. Nitrogen sorption measurements at 77 K were performed on a Micromeritics ASAP 2020 instrument. The samples were degassed at 200°C during 12h prior to analysis.

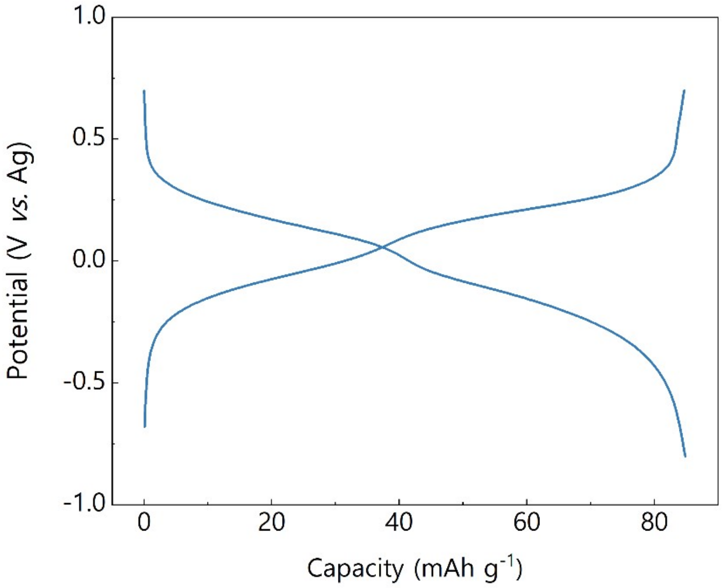
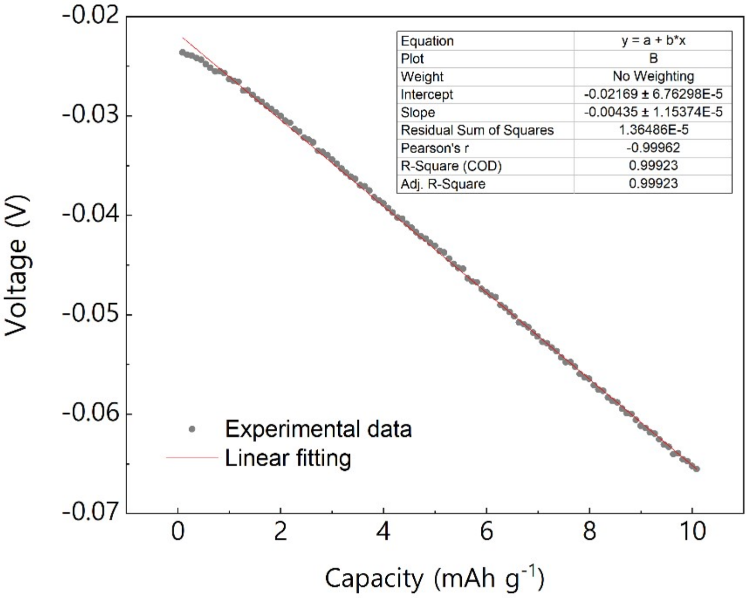


Figure S1. Galvanostatic charge-discharge profile of Ca-Zn-PTtSA electrode measured in a three-electrode Ca-Zn-PTtSA || Ag || activated carbon cell, using 0.5M Ca(TFSI)$_2$/PC electrolyte and a current density of 10 mA g^{-1}.



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-0.02169 ± 6.76298E-5
Slope	-0.00435 ± 1.15374E-5
Residual Sum of Squares	1.36486E-5
Pearson's r	-0.99962
R-Square (COD)	0.99923
Adj. R-Square	0.99923

Figure S2. Galvanostatic discharge profile of AC electrode measured in a two-electrode AC || AC cell, using 0.5M Ca(TFSI)$_2$/PC electrolyte at a current density of 10 mA g^{-1}, together with the linear mathematical fitting used to determine the slope.

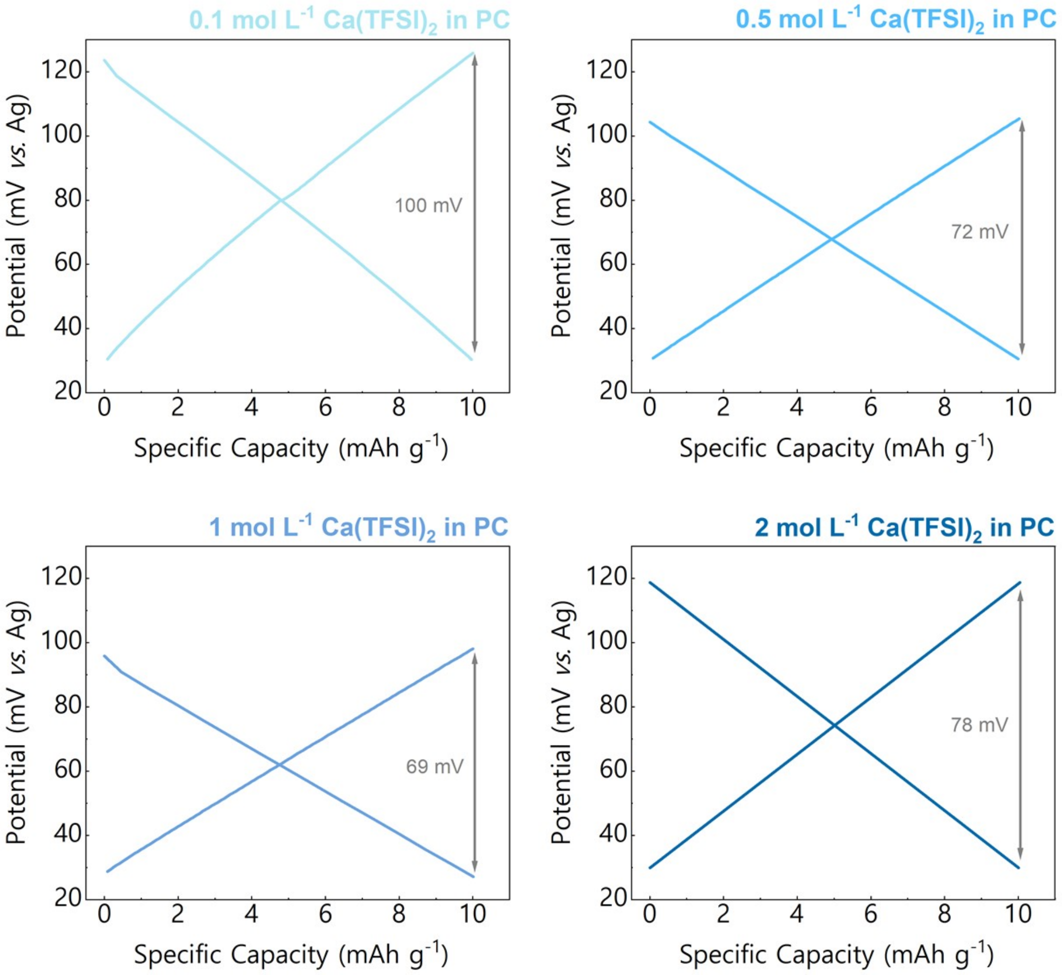


Figure S3. Galvanostatic charge-discharge profiles of activated carbon cloth counter electrode measured in a symmetric activated carbon || Ag || activated carbon three-electrode cell, using propylene carbonate electrolytes with different Ca(TFSI)$_2$ concentration.

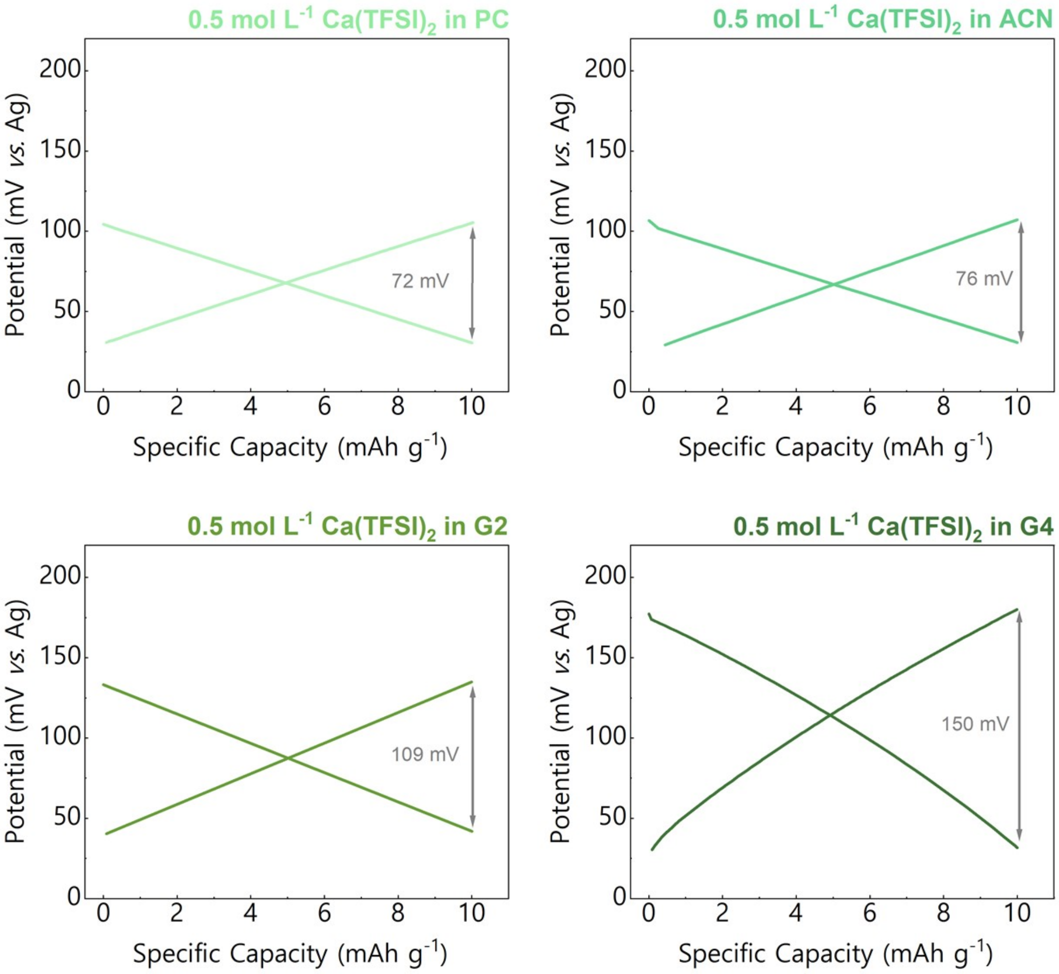


Figure S4. Galvanostatic charge-discharge profiles of activated carbon cloth counter electrode measured in a symmetric activated carbon || Ag || activated carbon three-electrode cell, using 0.5 mol L^{-1} $Ca(TFSI)_2$ in different solvent electrolytes.

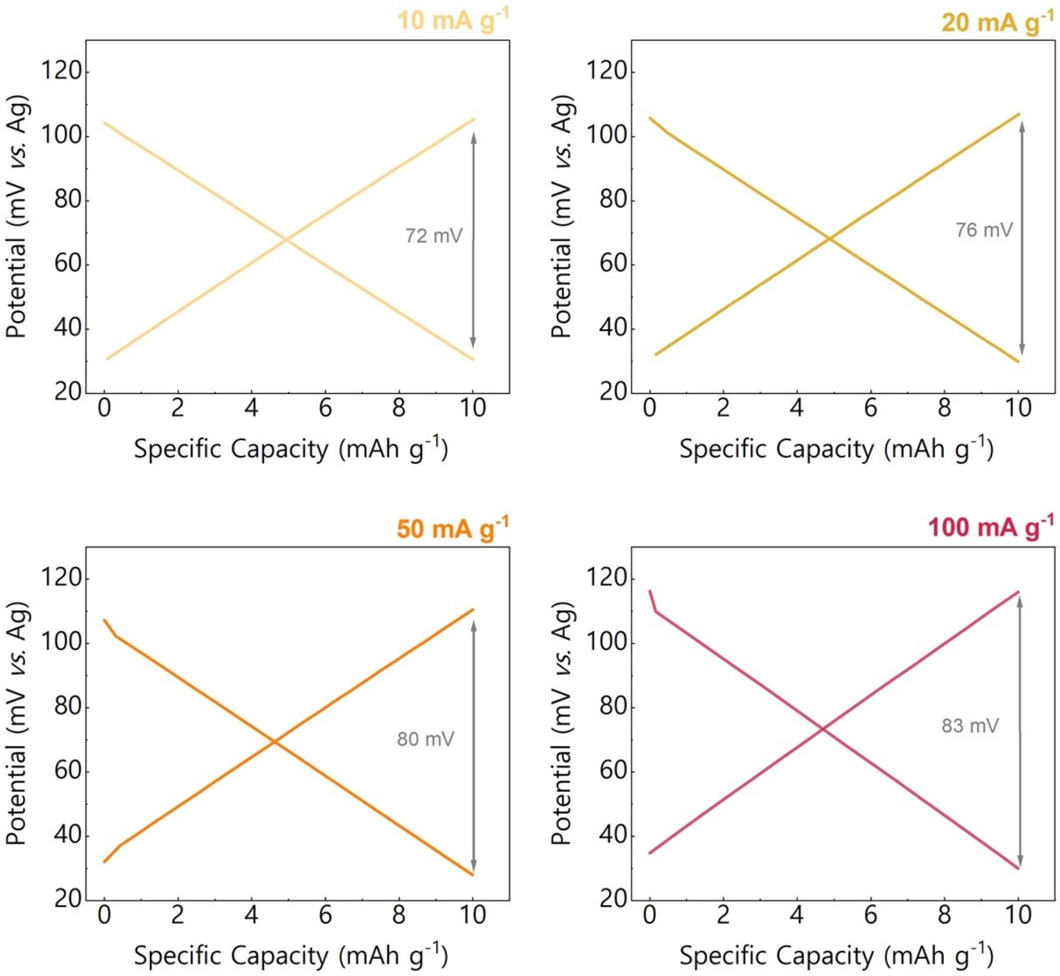


Figure S5. Galvanostatic charge-discharge profiles of activated carbon cloth counter electrode measured in a symmetric activated carbon || Ag || activated carbon three-electrode cell, with 0.5 mol L^{-1} $Ca(TFSI)_2$ in propylene carbonate and cycled at different current density.

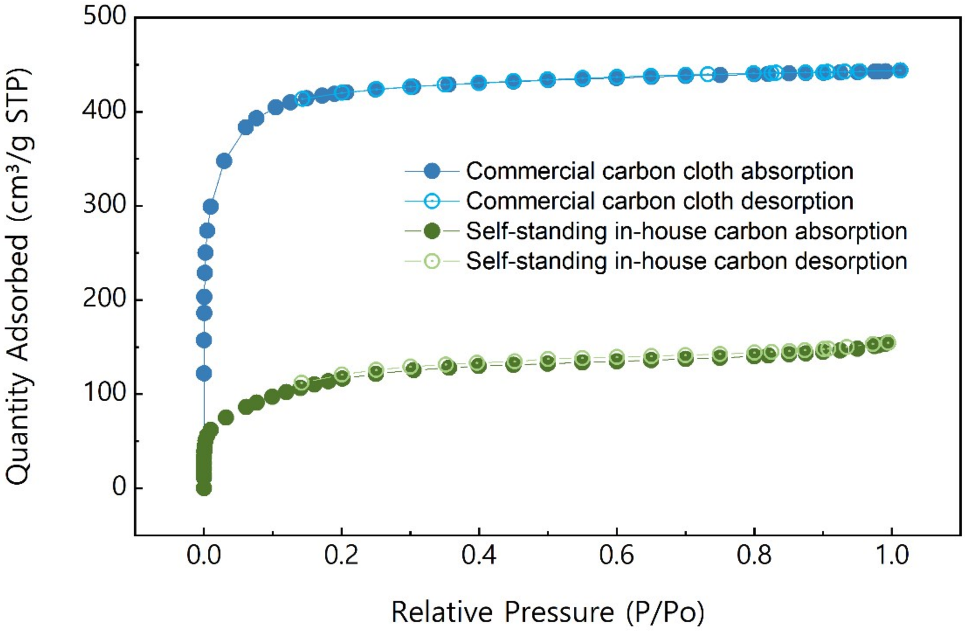


Figure S6. N_2 adsorption-desorption isotherms for commercial carbon cloth and self-standing in-house carbon measured at 77K.

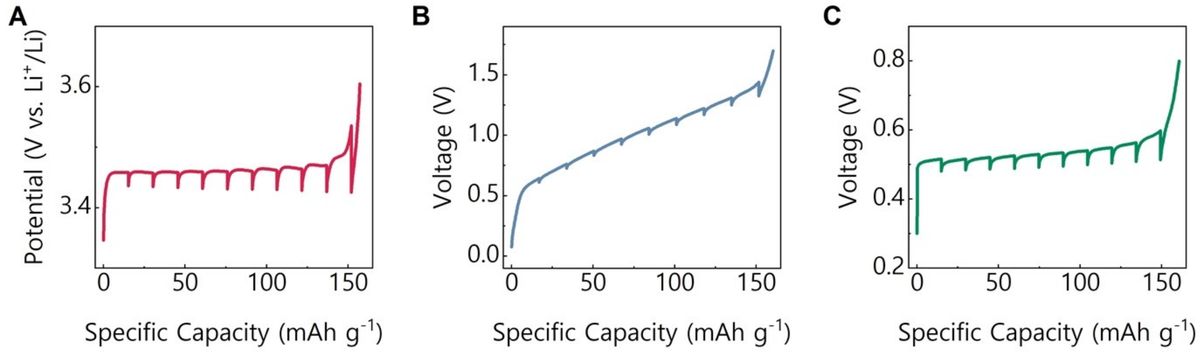


Figure S7. GITT curves of the LFP electrode during the second galvanostatic charge cycle in two-electrode cells: (A) LFP||Li metal, (B) LFP||AC (1:5 LFP-to-AC mass ratio), and (C) LFP||AC (1:30 LFP-to-AC mass ratio). The cells were cycled at a current density of 15 mA g^{-1} in 1M $LiPF_6$ in EC:DMC electrolyte. 5 h OCV relaxation period follows each galvanostatic charge collection or injection for a duration of 1 h.