Supporting Information

Enhanced Fast Charging Capabilities in Natural Graphite/Iron Cross-Linked Pectin Electrodes for Lithium-Ion Batteries

Chin-Yi Chung[a, b, c], Wei-Ming Chen[a, b, c], Yan-Ruei Chen[a, b, c], Liang-Yu Chen[a], Yu-Hsuan Su[a, b, c], Po-Wei Chi[a]*, Phillip M. Wu[a, d]*, Kuei-Shu Chang-Liao[c], Hong-Yi Tang[e] and Maw-Kuen Wu[a]

[a]Institute of Physics, Academia Sinica
128, Section 2, Academia Road, Taipei 11529, Taiwan.

[b]Nano Science and Technology Program, Taiwan International Graduate Program, Academia Sinica and National Tsing Hua University
128, Section 2, Academia Road, Taipei 11529, Taiwan.

[c]Department of Engineering and System Science, National Tsing Hua University
101, Section 2, Kuang-Fu Road, Hsinchu 300044, Taiwan.

[d]College of Science, National Chung Hsing University
145, Xingda Road, South District, Taichung 402, Taiwan.

[e]Department of Applied Chemistry, National Chi-Nan University
 1 University Road, Puli, Nantou, 545301, Taiwan

*Corresponding author

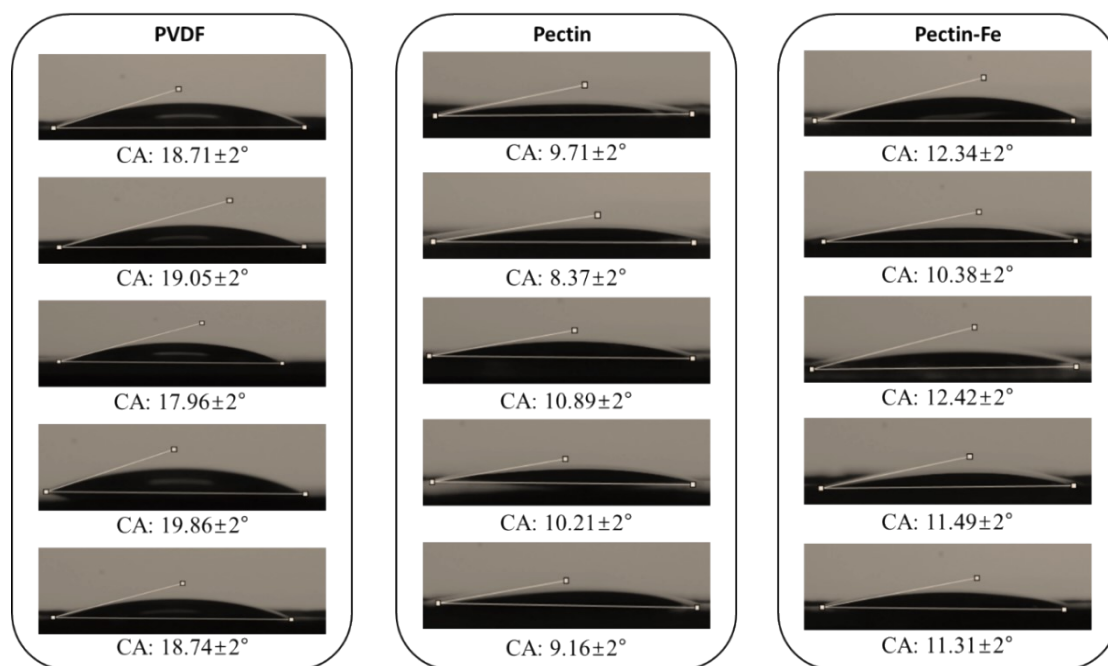**philwu@gmail.com** and **poweichi@gate.sinica.edu.tw**

Figure S1. Contact angle images of PVDF, pectin, and pectin:Fe electrodes.
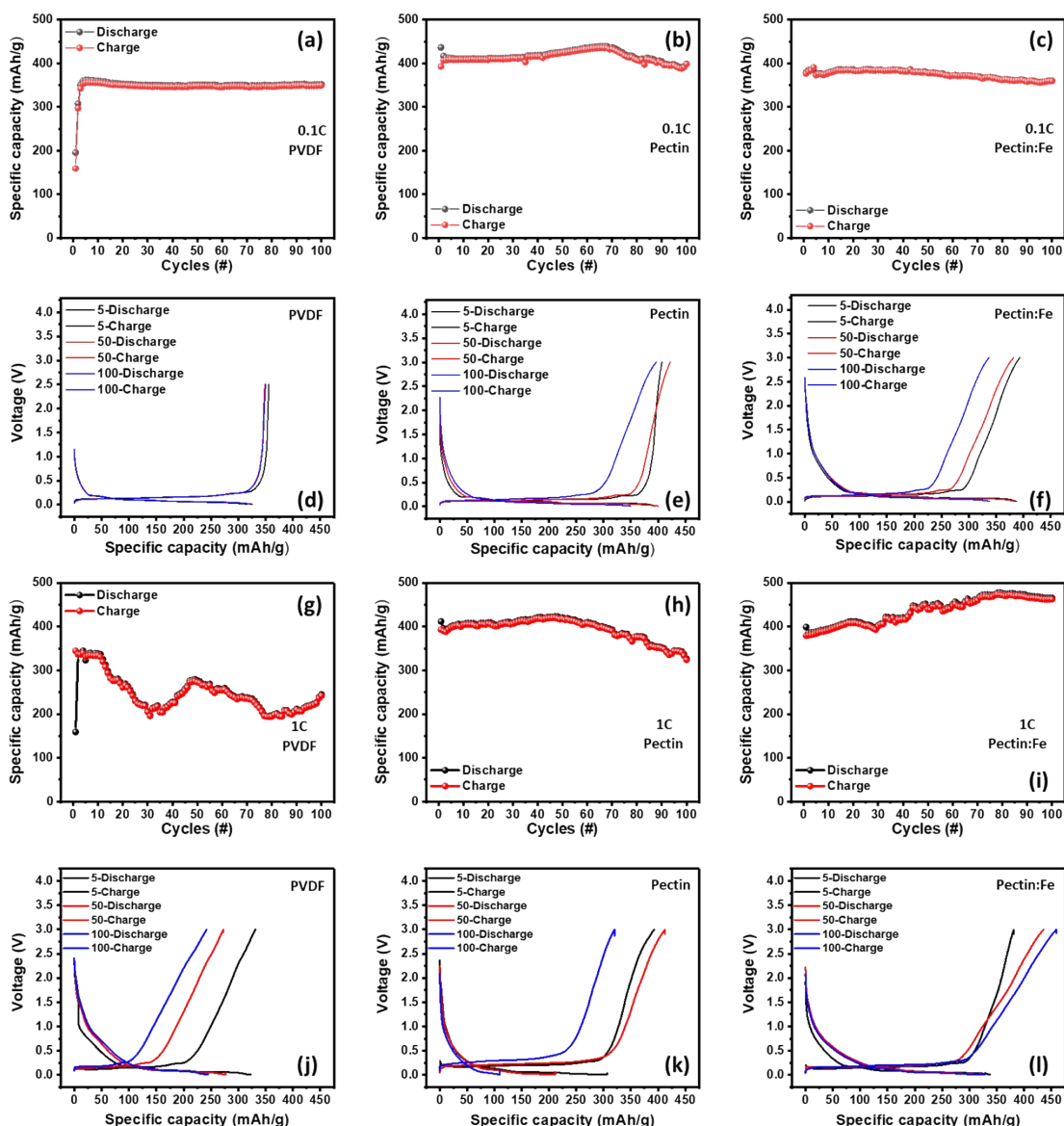
Figure S2. Cycling performance for (a) graphite-PVDF, (b) graphite-pectin, and (c) graphite-pectin:Fe electrodes under 0.1 C within the potential range from 0.01 V to 3V. The corresponding voltage profiles are shown in (d)-(f). Additionally, (g)-(i) show the cycling performance for graphite-PVDF, graphite-pectin, and graphite-pectin:Fe electrodes, respectively, under 1 C within the potential range from 0.01 V to 3V, with corresponding voltage profiles displayed in (j)-(l).

Analysis of electrochemical kinetics

CV is a powerful technique used to evaluate the electrochemical reaction kinetics of active materials with Li ions. It provides essential information on redox couples, potential ranges for chemical reactions, and overpotential, inferred from the positions and intensities of the cathodic and anodic peaks.

In a CV experiment, the current response (i) as a function of the sweep rate (v) reveals insights into the charge-storage process. This relationship can be described by the following power law expression:

$$i(v)=av^b \text{---(eq. 1)}$$

where a is a constant and b is the power-law exponent. The b value can be determined from the slope of the log-log plot of current ($\log(i)$) versus sweep rate ($\log(v)$) for the cathodic and anodic peaks. Based on the experimentally derived b values, the charge storage mechanism can be qualitatively assessed. Specifically, a b value close to 0.5 indicates a diffusion-controlled process, while a b value close to 1 suggests a surface-controlled (capacitive) process.

If $b=1$ or 0.5, then the equation can be rewritten as

$$i=k_1v \text{ or } i=k_1v^{1/2} \text{ ---(eq. 2)}$$

When two different lithiation mechanisms occur simultaneously, they can be quantitatively distinguished and modeled by combining their respective contributions. For instance, if both surface-controlled (capacitive) and diffusion-controlled processes are present, the total current response can be expressed as a combination of both mechanisms:

$$i=k_1v+k_1v^{1/2} \text{ ---(eq. 3)}$$

After dividing the equation by $v^{1/2}$,

$$i/v^{1/2}=k_1 v^{1/2}+k_2 \text{ ---(eq. 4)}$$

In eq. 4, k_1 and k_2 represent the current contributions between the capacitive response on the surface and the diffusion-controlled process, respectively. Therefore, we can quantify the fraction of current at certain potentials from a simple calculation of k_1 and k_2.
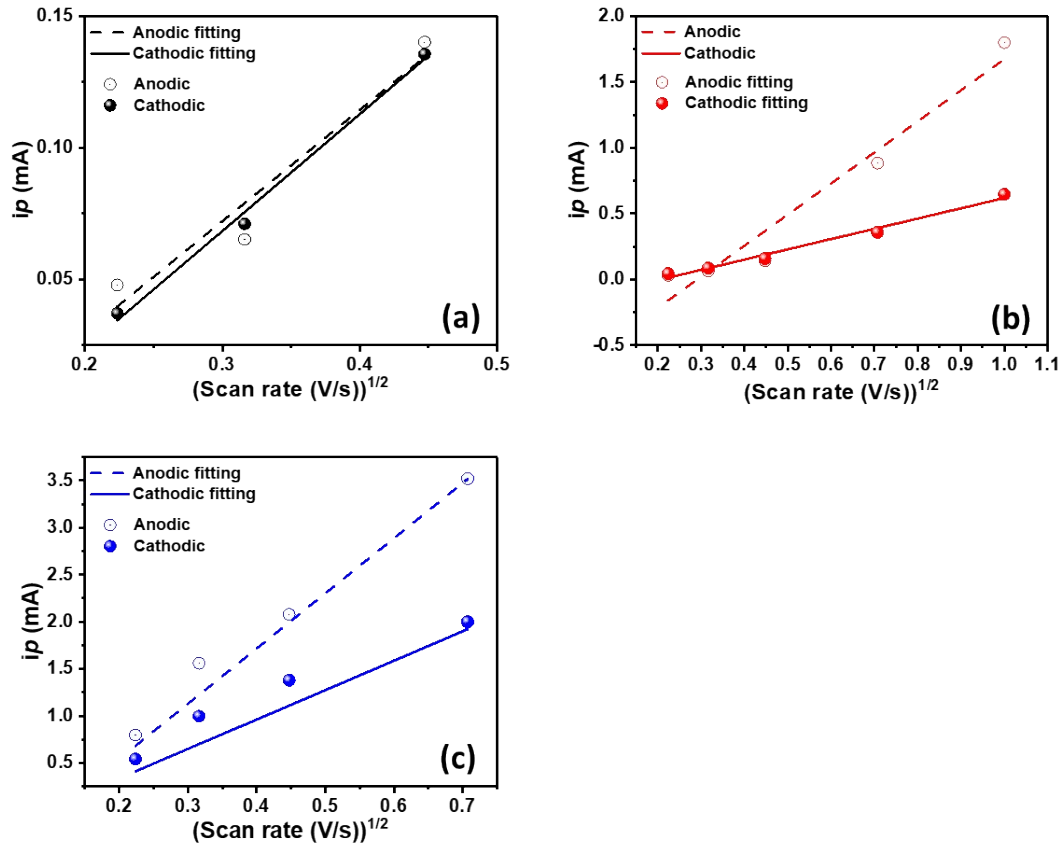
Figure S3. Dependence of anodic and cathodic peak currents (I) on the square root of the scan rate for (a) graphite-PVDF, (b) graphite-pectin, and (c) graphite-pectin:Fe electrodes.

Figure S3 shows a linear relationship between each redox peak current (Ip) and the square root of the scan rate ($v^{1/2}$), as expected for the diffusion-limited cathodic/anodic processes of Li-ion. Subsequently, we applied the classical Randles-Sevchik equation to investigate the semi-infinite diffusion of Li$^+$ into graphite-PVDF, graphite-pectin, and graphite-pectin:Fe electrodes. This equation is derived from the adsorption process theory at the metal/solution interface [1]

$$I_{\mathrm{p}} = (2.69 \times 10^5) n^{3/2} S D_{Li^+}^{1/2} C_{Li}^* v^{1/2}$$ ---(eq. 5)

where Ip is the peak current (mA), n is the charge-transfer number, S is the contact area between the electrode and electrolyte (1.54 cm^2), D$_{Li+}$ is the chemical diffusion coefficient of lithium ions (cm^2 s$^{-1)}$, C$_{Li}$ is the concentration of lithium ions in the anode material, and v is the potential scan rate (V s^{-1}).
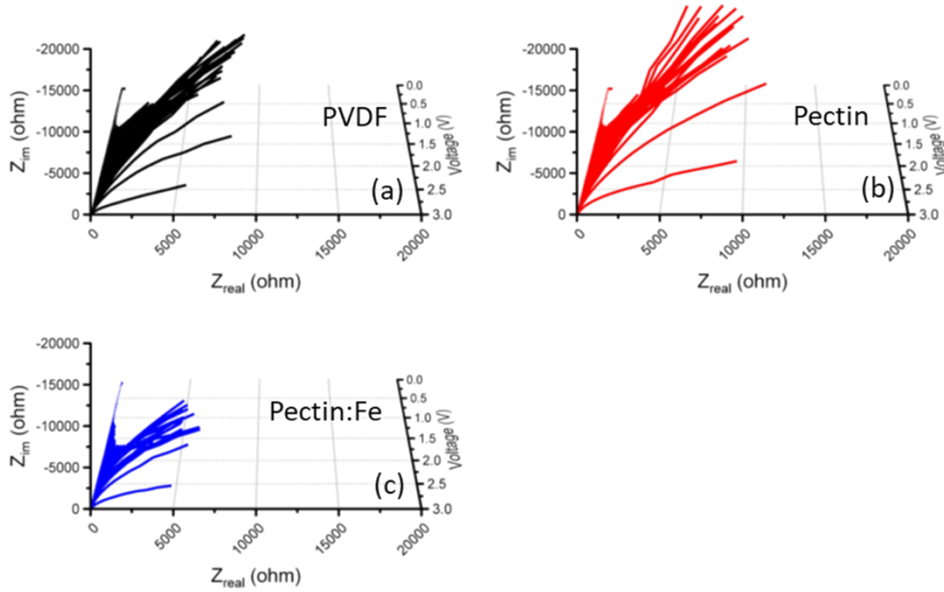
Figure S4. EIS spectra of (a) graphite-PVDF, (b) graphite-pectin, and (c) graphite-pectin:Fe electrodes. All plots collected from 3 V to 0.01 V, while data collection occurred over a frequency range of 0.5 mHz to 100 kHz at each voltage step.

To prepare 3D Bode plots, impedance cycling was performed at 10 mV intervals, starting from 3 V to 0.01 V, while data collection occurred over a frequency range of 0.5 mHz to 100 kHz at each voltage step. Before conducting impedance cycling, all cells were activated using preconditioning steps that involved performing cyclic voltammetry at a scan rate of 0.1 mV s^{-1} across a potential range of 0.01 V to 3 V for three cycles. Data were collected across the entire voltage range at 50 mV increments. The impedance data can be shown in the form of Bode plots, where the phase angle (ϕ) or capacitance (C) is represented as a function of frequency. In this study, we focused on measurements in the low-frequency range (5 mHz-1 Hz), where these electrodes mainly exhibit a capacitive response. This behavior was explained by Taberna *et al.* [2], who developed a simple series resistor-capacitor circuit to calculate the impedance of carbon-based electrochemical capacitors. Both components exhibited a frequency-dependent response. According to these assumptions, the real and imaginary components of the capacitance (C' and C'', respectively) can be obtained by employing equations (6) and (7) in relation to the angular frequency (ω).

$$C' \frac{-Z''(\omega)}{\omega |Z(\omega)|^2}$$ --(eq. 6)

$$C'' \frac{Z'(\omega)}{\omega|Z(\omega)|^2}$$ --(eq. 7)
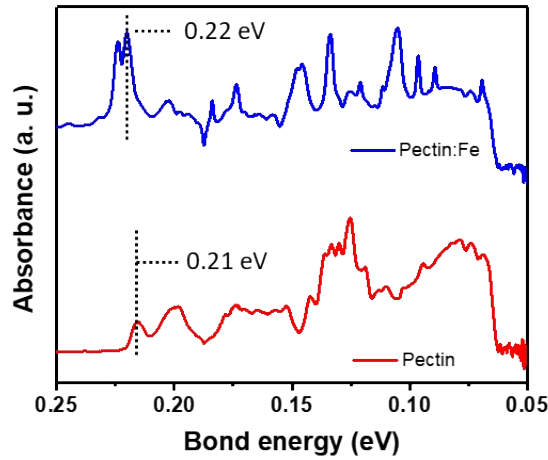

Figure S5. Comparison of FTIR spectra of pectin (red line) and pectin:Fe (blue line) electrodes.

Richard M. Badger presented a revised version of formula (eq. 8) for determining the bond length (R) based on the force constant k (dynes.cm^{-1}), as demonstrated in the equation below: **[3, 4]**

$$R = \sqrt[3]{\frac{C_{ij}}{k}} + d_{ij}$$ --(eq. 8)

where k is the force constant in mega-dynes per centimeter (1 Nm^{-1} = 0.001 Md.cm^{-1}). The values of C_{ij} and d_{ij} depend on the number of bonded atoms in the periodic table for a given period. For Fe-COO, the value of C_{ij} is 0.5, and d_{ij} is 1.06 Å.

Hook's law was employed to calculate the force constant (k) of the bond by employing the fundamental harmonic (eq. 9), which serves as an indicator of bond stiffness. Notably, shorter bonds are generally stronger and have a higher force constant (k).

$$v = \frac{1}{2\pi c}\sqrt{\frac{k}{u}}$$ ---(eq. 9)

where u is the reduced mass (kg) of the bonded atoms and is determined using the relation given in eq. 10:

$$u = \frac{m1 \times m2}{m1 + m2}$$ ---(eq. 10)

where $m1$ and $m2$ are the atomic masses of the bonded atoms.

The following is used to manipulate eq. 9 and obtain the force constant (k, Nm^{-1}) from wavenumbers (cm^{-1}) as shown in eq. 11

$$k = v^2 4\pi^2 c^2 u \text{---(eq. 11)}$$
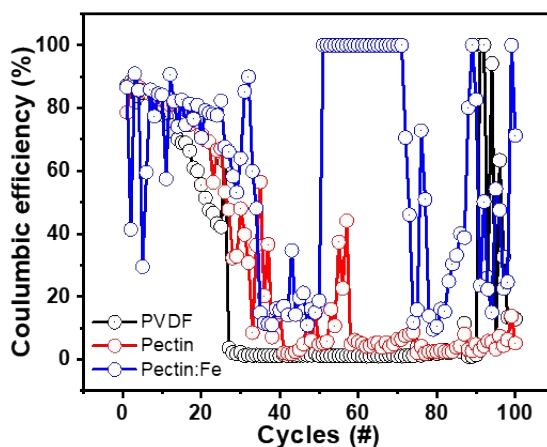

Figure S6. Coulombic efficiency of the Li platting/stripping process on the graphite-PVDF, graphite-pectin, and graphite-pectin:Fe electrodes, each with a deposition capacity of 1 mAh cm^{-2} and a current of 1 mA cm^{-2}.

Reference

[1]   Tang, S. B., *et al.* "Study on Li$^+$-Ion Diffusion in Nano-crystalline LiMn$_2$O$_4$ Thin Film Cathode Grown by Pulsed Laser Deposition Using CV, EIS and PITT Techniques." *Mater. Chem. Phys.*, vol. 111, 2008, p. 149.

[2]   Taberna, P. L., *et al.* "Electrochemical Characteristics and Impedance Spectroscopy Studies of Carbon-Carbon Supercapacitors." *J. Electrochem. Soc.*, vol. 150, 2003, pp. A292-A300.

[3]   Kaupp, M., *et al.* "Chemistry is about energy and its changes: A critique of bond-length/bond-strength correlations." *Coord. Chem. Rev.*, vol. 344, 2017, pp. 355-362.

[4]   Badger, R. M. "The relation between the internuclear distances and force constants of molecules and its application to polyatomic molecules." *J. Chem. Phys.*, vol. 3,

1935, pp. 710-714