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Supporting Information for

Green water-based binders for $LiFePO_4/C$ cathode in Li-ion batteries: a comparative study

Xiaojing Zhang, Xinyi Ge, Zhigang Shen, Han Ma, Jingshi Wang, Shuai Wang, Lei Liu, Beibei Liu, Lixin Liu, Yizhi Zhao

We employ the measured values (not fitting) of EIS to calculate the Warburg coefficient σ and Li-ion diffusion coefficient (D_{Li^+}).

The Warburg coefficient σ can be calculated by equation 1

$$|Z'| = R_b + R_{ct} + \sigma \omega^{-1/2}$$ Equation 1

Here, ω is the angular frequency in the low frequency region.

D_{Li^+} can be calculated by the equation 2

$$D_{Li^+} = \frac{R^2T^2}{2An^4F^4C^2\sigma^2}$$

Equation 2

Here, R, T, A, n, F and C correspond to the gas constant (8.314 J mol^{-1} K^{-1}), the absolute temperature (298.15 K), the area of the cathode interface (1.12 cm^2), Faraday constant (96485 C mol^{-1}), the charge transfer number (1) and molar concentration of the lithium ions (0.0228 mol cm^{-3}), respectively. The Warburg coefficient σ and the D_{Li^+} of all samples are listed in Table S1.

As illustrated in Fig. S1, for E-SA, E-CMC/SA, E-CMC/SBR and E-PAA, there are more than 10 dots in the straight line of the low frequency region, which provide the little fitting error and the data reliability. Meanwhile, for E-CMC, E-PVDF, E-CMC/PAA and E-CMC/PTFE, the number of dots in the straight line is a little less. Therefore, in the fitting of straight slope, we choose 5 dots, which maybe result in a little bigger error. However, the difference in an order of magnitude is still sufficient to demonstrate the variation of Li^+ transport velocity (e.g., the D_{Li^+} value of SA and PVDF are 16.3×10^{-15} cm^2S^{-1} and 3.2×10^{-15} cm^2S^{-1} respectively). Furthermore, no values of D_{Li^+} show big difference lower than PVDF, which can demonstrate that the green water-based binders didn't have a negative effect on Li^+ transport.

In addition, considering the errors mentioned above, we investigated the apparent diffusion coefficient of Li^+ (D_{app}) calculated from the CV measurement for supporting. The D_{app} was calculated based on the Randles-Sevcik equation

$$i_P = 0.4436F\left(\frac{F}{RT}\right)^{1/2}C^*v^{1/2}AD^{1/2}$$

Equation

3

where i_p, F, R, T, C*, v, A and D are the peak current in amperes, the Faraday constant (96485 C mol^{-1}), the universal gas constant (8.314 J $mol^{-1}K^{-1}$), temperature (K), the initial concentration in mol cm^{-3}, the scan rate in Vs^{-1}, the electrode area in cm^2, and the diffusion constant in cm^2s^{-1}, respectively. The equation could be written at 25℃ as

$$\frac{i_p}{m} = 2.69 \times 10^5 C_{Li}^* v^{1/2} A_e D_{app}^{1/2}$$

Equation 4

where m is the electrode mass in g, C_{Li}^* is the initial concentration of Li in LFP in mol cm^{-3} and is 0.0228 mol cm^{-3} here, A_e is the electrode area per unit mass in cm^2g^{-1} and is taken as the effective area of (010) plane which is 15.1 m^2g^{-1}. D_{app} is the apparent diffusion constant of Li^+ in cm^2s^{-1}, m and i_p are obtained from the testing results.

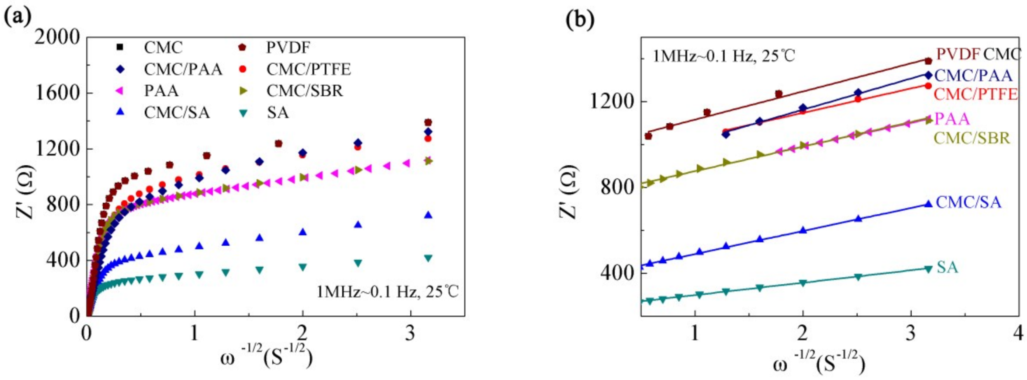

Fig. S1 (a) The curve from Equation 1, (b) The fitting of the straight line in the low frequency region

Table S1 The results obtained from the EIS and CV measurements

Binder	Discharge Capacity (mAh/g, 2C, average)	σ (Ω cm^2 $S^{0.5}$)	D_{Li^+} ($\times10^{-15}$ cm^2 s^{-1})	D_{app} ($\times10^{-15}$ cm^2 s^{-1})

SA	140.5	57.8	16.3	9.4
CMC/PTFE	141.2	113.6	4.2	6.8
CMC/SA	131.8	107.3	4.7	3.3
CMC	129.2	131.1	3.2	1.9
PAA	119.4	110.0	4.5	1.0
CMC/SBR	127.3	114.6	4.1	0.5
CMC/PAA	121.9	145.2	2.6	1.1
PVDF	134.6	131.1	3.2	0.65

As shown in table S1, for E-SA, both the D_{Li^+} and D_{app} are several times higher than E-PVDF, indicating that E-SA has the better kinetical capability, which match the discharge capacity at 2C. For E-CMC/PTFE, the D_{Li^+} value from EIS is equivalent to E-PVDF, but the D_{app} value from CV is ten times higher than E-PVDF, and the discharge capacity at 2C is higher as well. Considering the error of D_{Li^+}, it can be concluded that E-CMC/PTFE has the enhanced kinetical capability than E-PVDF. For the other electrodes with water-based binders, compared with E-PVDF, there are no big differences in the D_{Li^+} and D_{app}, which can demonstrate that the kinetical capability of electrodes with water-based binders are not inferior to E-PVDF.

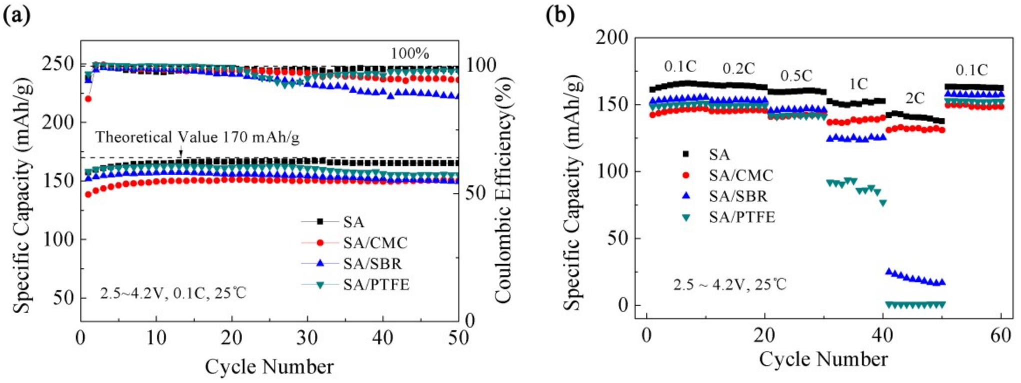

Fig. S2 Electrochemical performance of LFP/C electrodes with binder couples with SA, (a) cycle performance, (b) rate performance

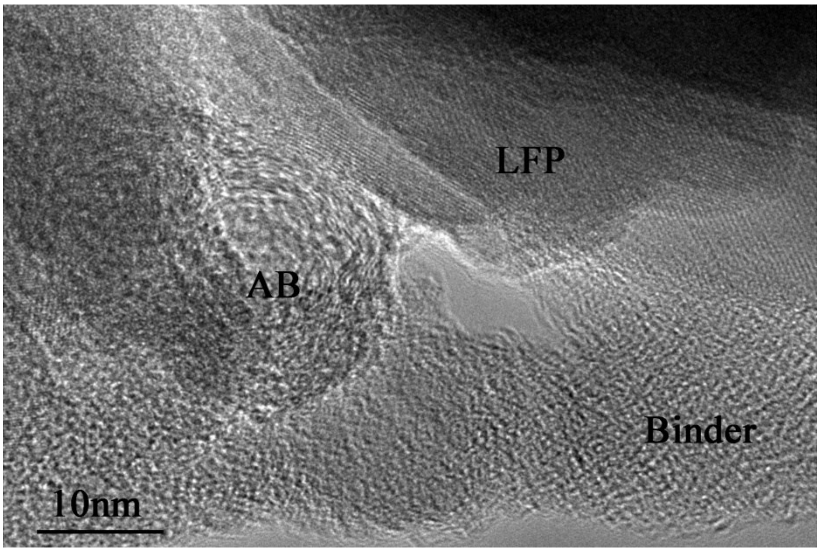

Fig. S3 HRTEM of electrode materials. LFP shows lattice fringe structure. AB shows annular structure. Binder (organic) shows undefined structure.

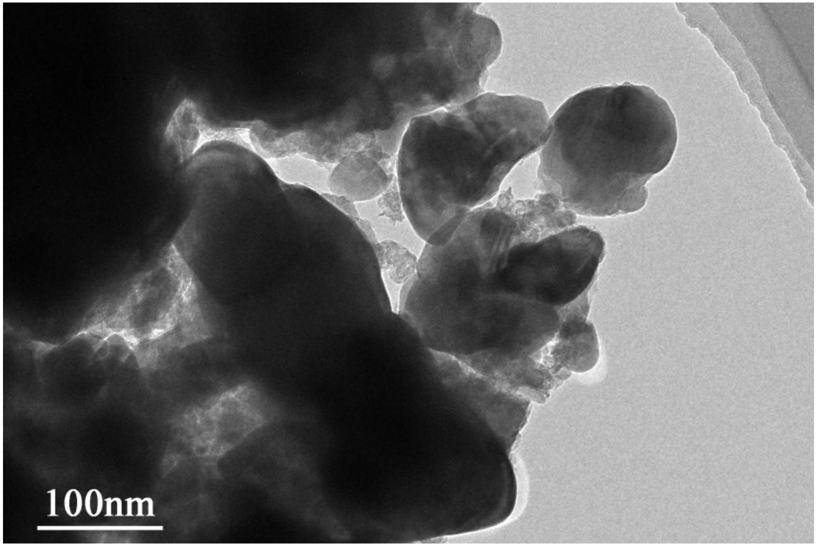

Fig. S4 The naked LFP in electrode