

Electronic Supplementary Information (ESI)

Chromium tetrphosphide (CrP₄) as a high performance anode for Li ion and Na ion batteries

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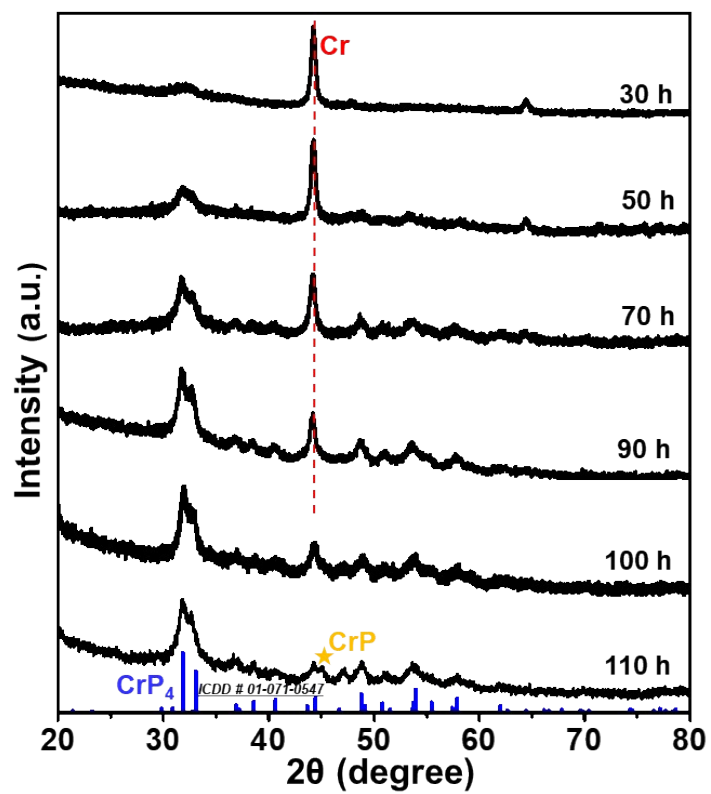


Fig. S1 XRD patterns of as-synthesized powder at different milling times.

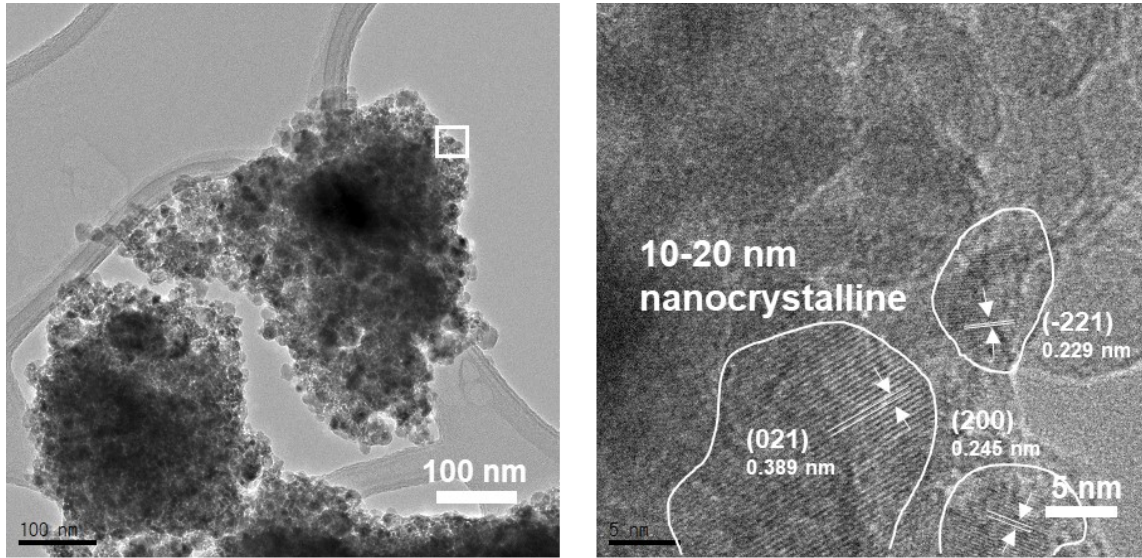


Fig. S2 TEM images of as-synthesized CrP₄ nanoparticles.

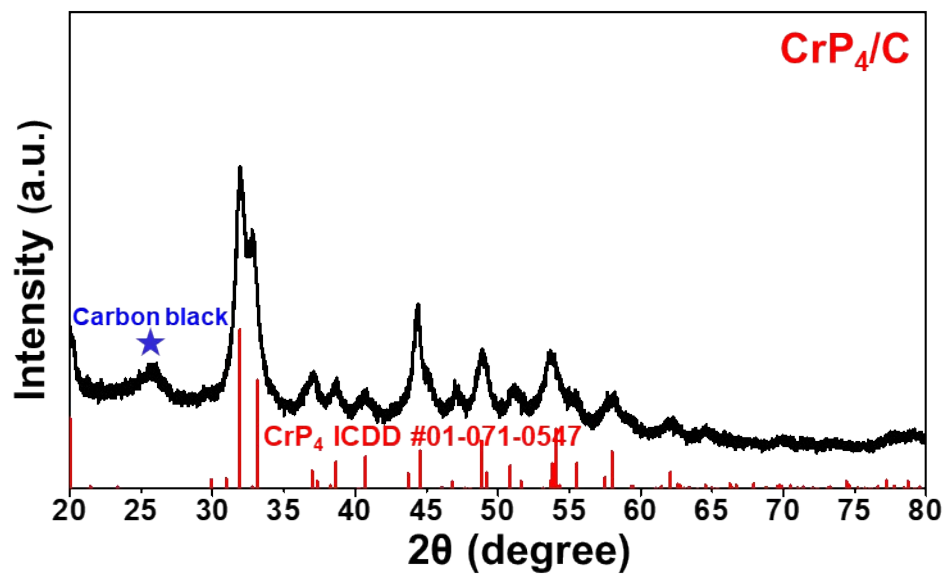


Fig. S3 XRD pattern of as-synthesized CrP₄/C nanocomposite.

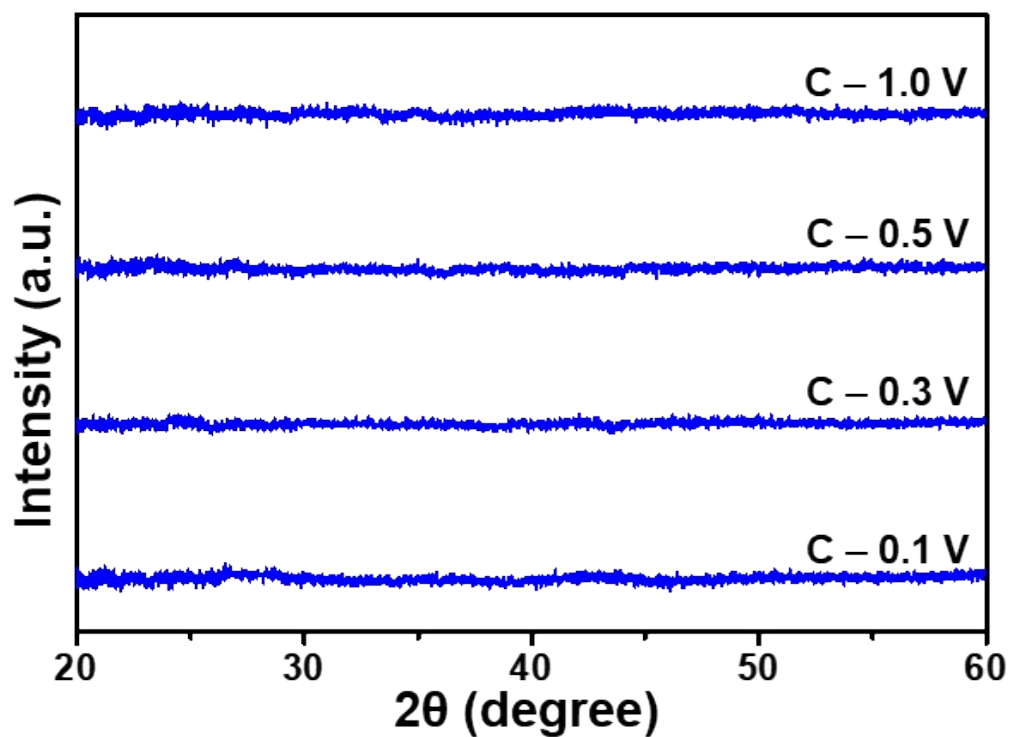


Fig. S4 *Ex-situ* XRD patterns of the CrP₄ electrode at various 1st charged states.

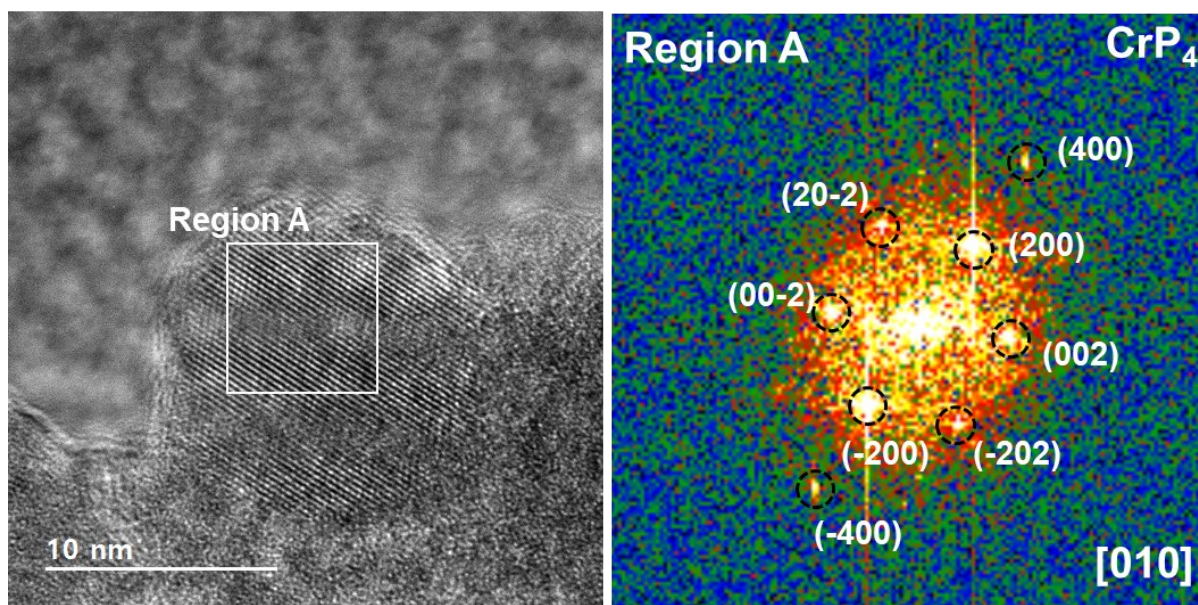


Fig. S5 HRTEM image and FFT pattern of the 1st fully charged (2.5 V vs. Li/Li⁺) CrP₄ electrode for LIBs.

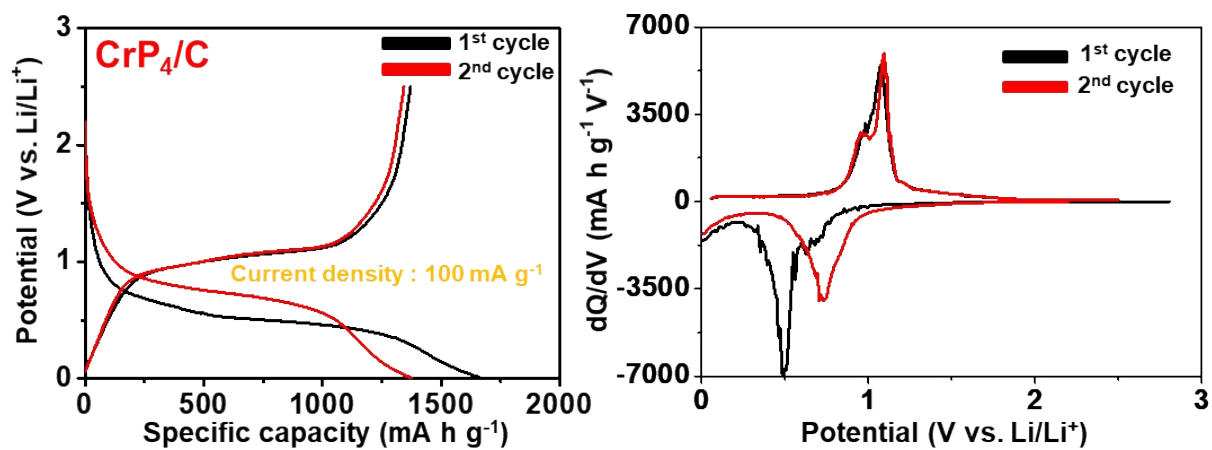


Fig. S6 Capacity-voltage profiles and corresponding DCPs of CrP₄/C electrode for LIBs at a current density of 100 mA g⁻¹.

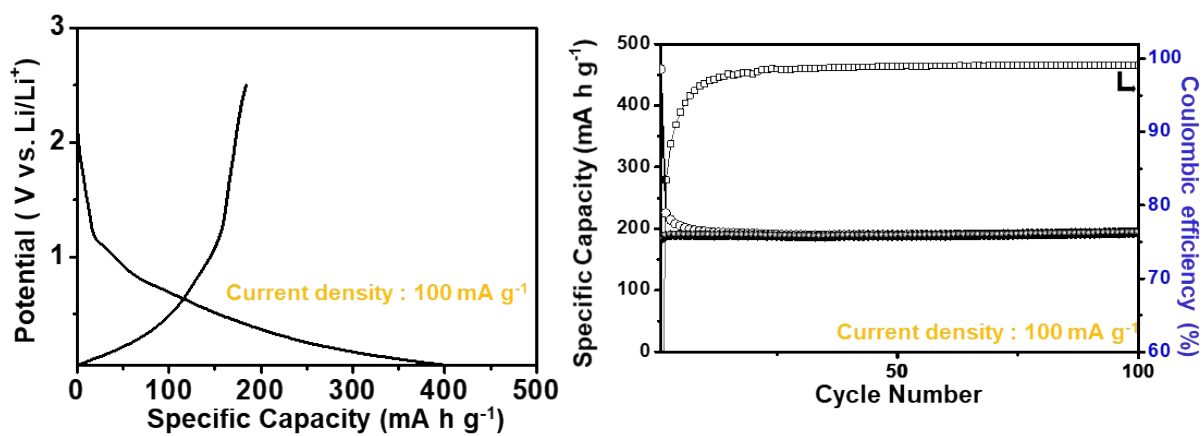


Fig. S7 Voltage profile and cycle performance of acetylene carbon black electrode for LIBs at a current density of 100 mA g⁻¹.

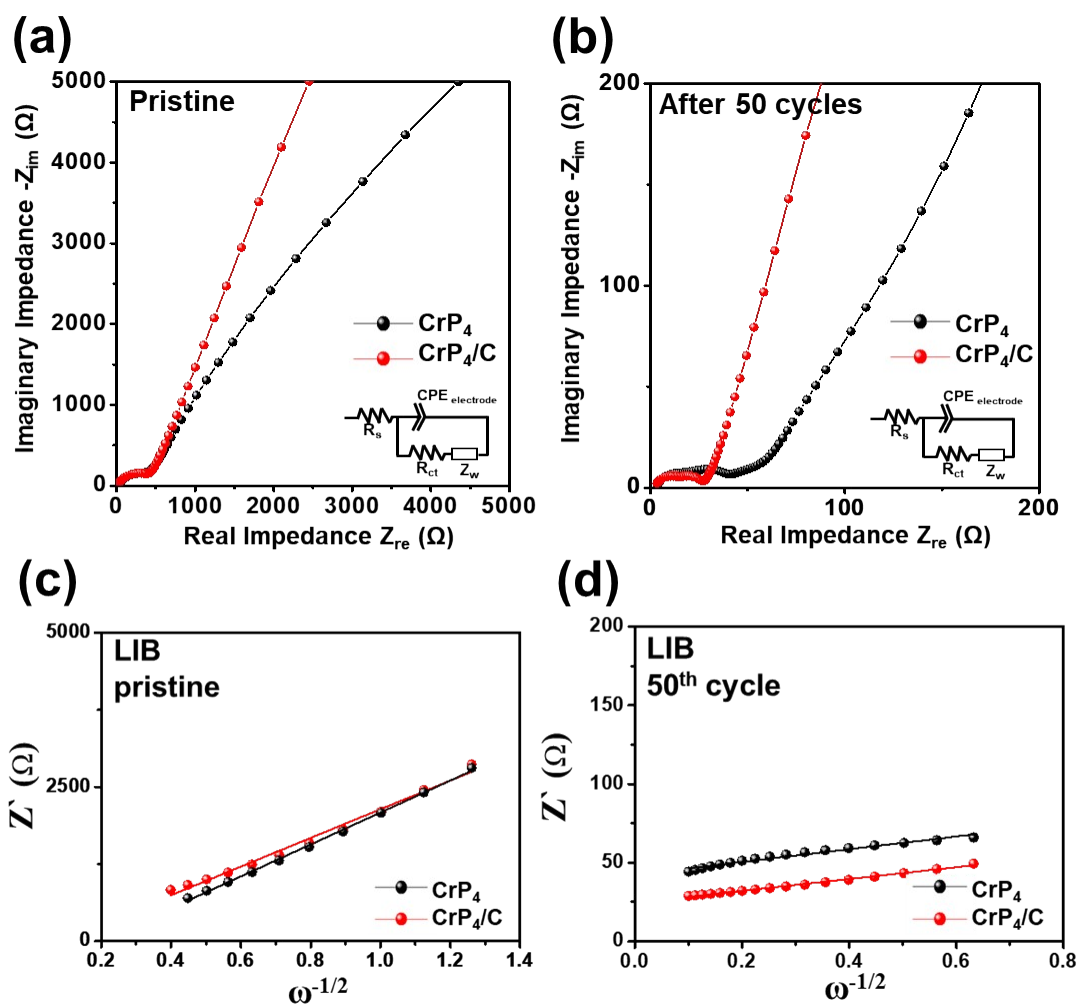


Fig. S8 Fitted Nyquist plots of CrP_4 and CrP_4/C electrodes (a) at pristine and (b) after 50 cycles and relationship between Z' and $\omega^{-1/2}$ (c) at pristine and (d) after 50 cycles at a current density of 1000 mA g^{-1} in LIBs.

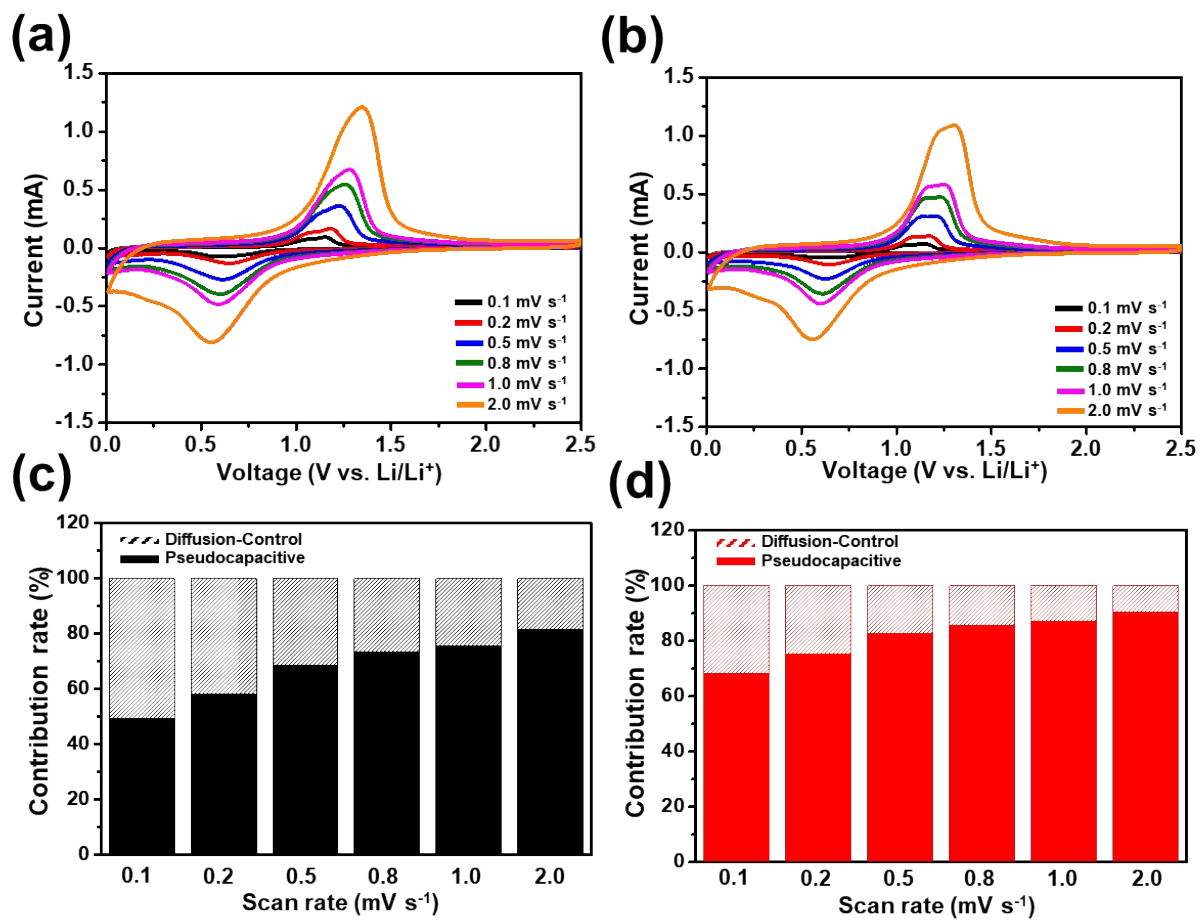


Fig. S9 CV curves and corresponding normalized contribution ratios of diffusion-controlled and pseudocapacitive-controlled at various scan rates from 0.1-2.0 mV s⁻¹ of (a, c) CrP₄ and (b, d) CrP₄/C electrodes in LIBs, respectively.

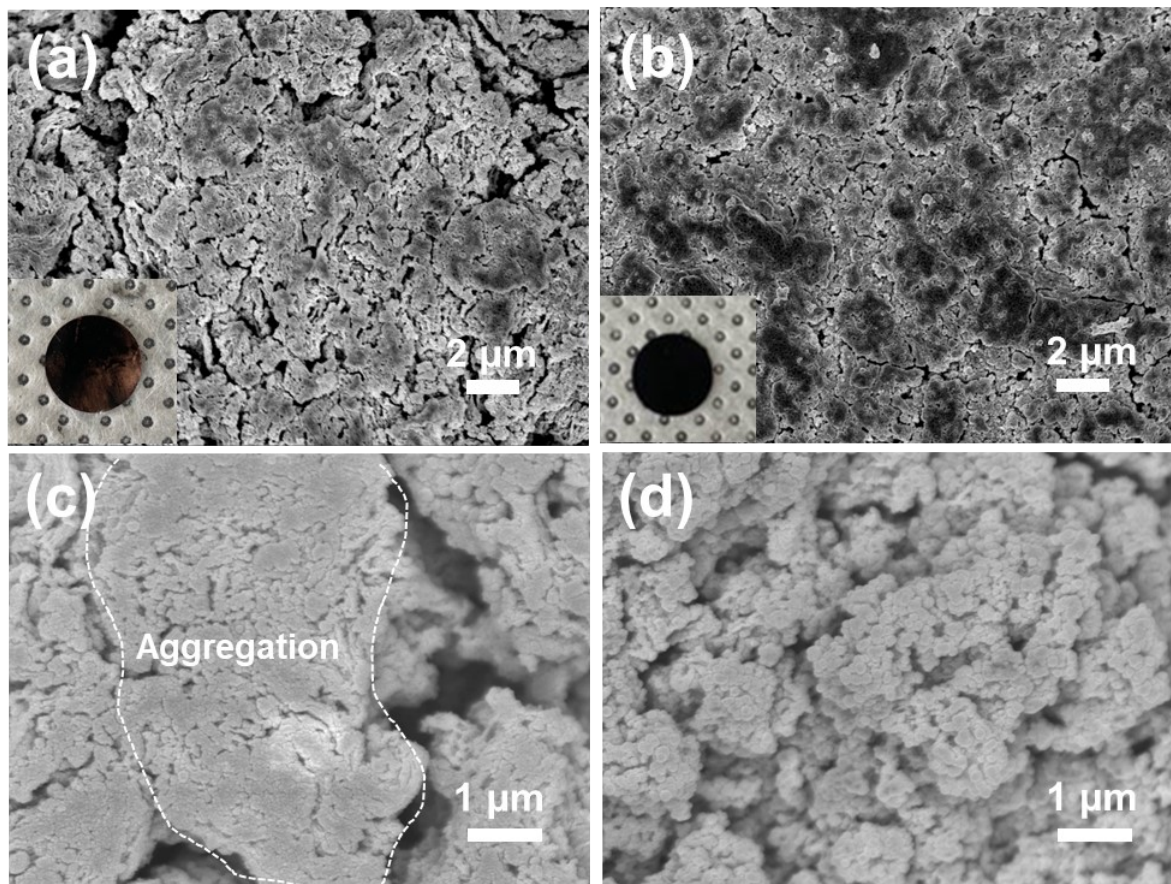


Fig. S10 SEM images of the electrodes before and after rinsing SEI layer of (a,c) CrP₄ and (b,d) CrP₄/C electrodes, respectively, after 50 cycles at a current density of 1000 mA g⁻¹ in LIBs (inset in (a) and (b): optical images of each electrodes).

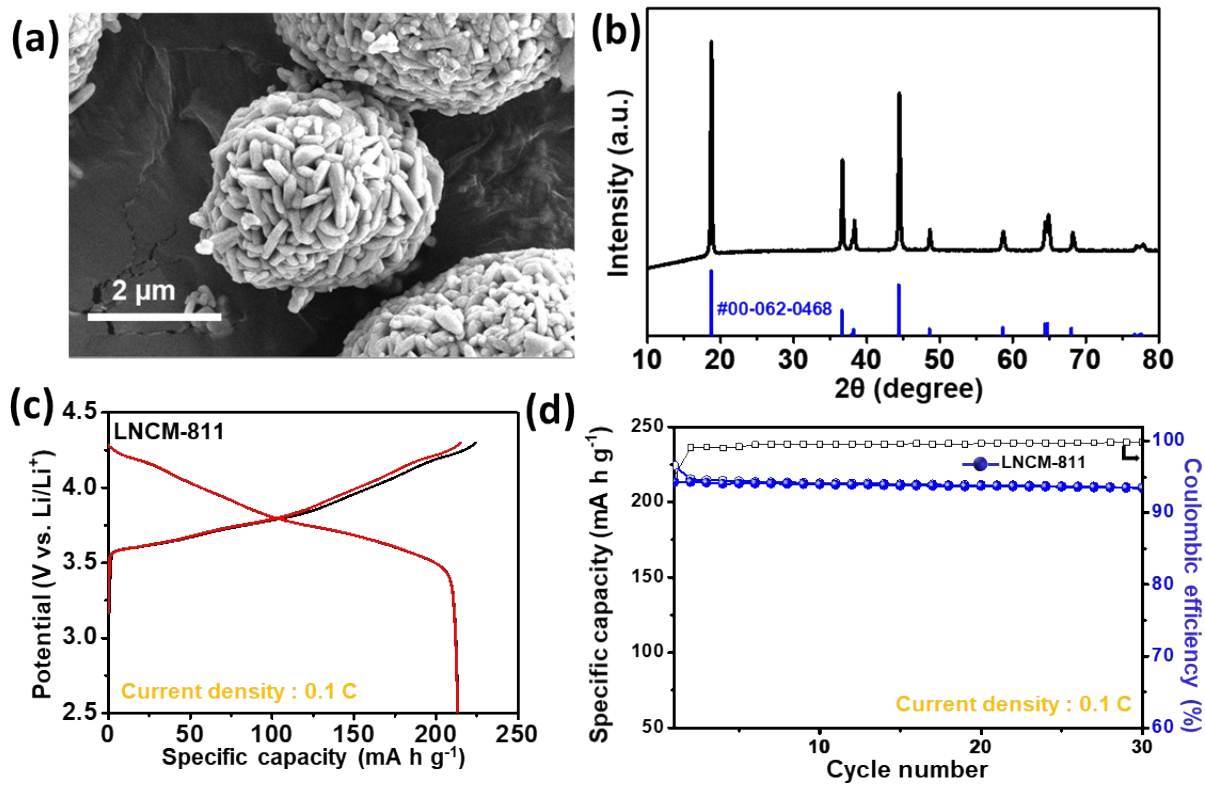


Fig. S11 (a) SEM image, (b) XRD pattern, (c) voltage profiles, and (d) cycle performance of the LNCM-811 cathode in LIBs at a current density of 0.1 C (20 mA g^{-1}).

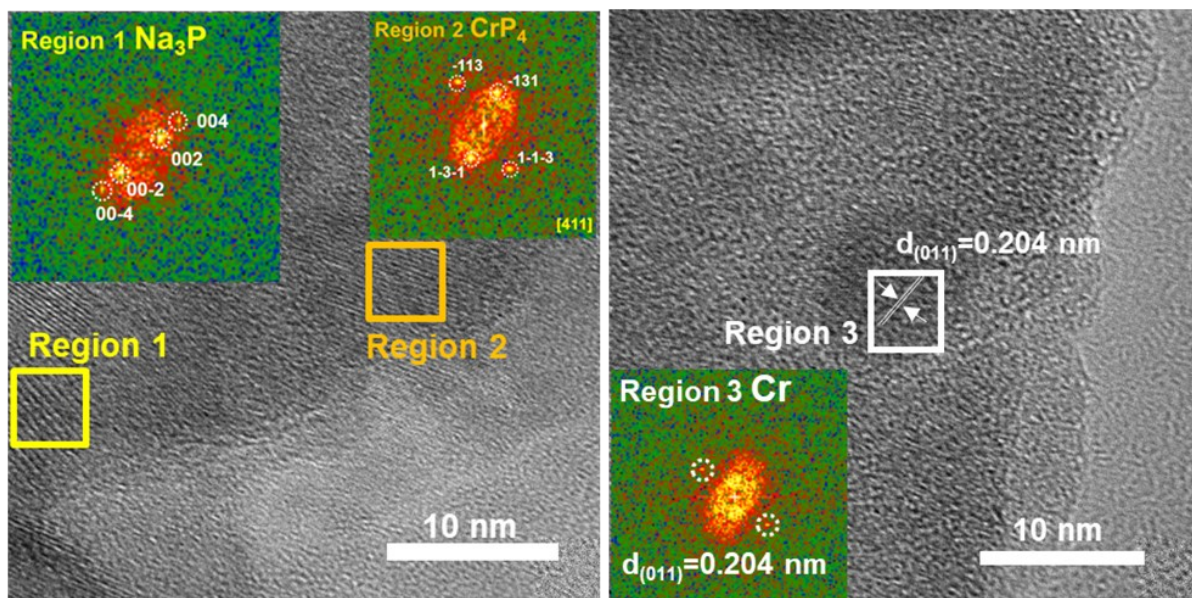


Fig. S12 HRTEM images and FFT patterns of the 1st fully discharged (0.01 V vs. Na/Na⁺) CrP_4 electrode in SIBs.

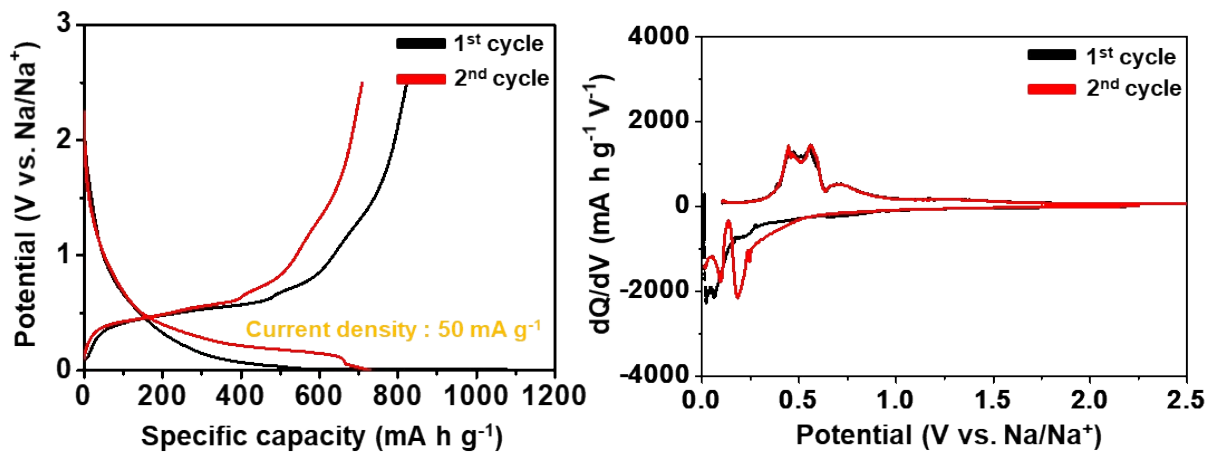


Fig. S13 Capacity-voltage profiles and corresponding DCPs of the CrP₄/C electrode in SIBs at a current density of 50 mA g⁻¹.

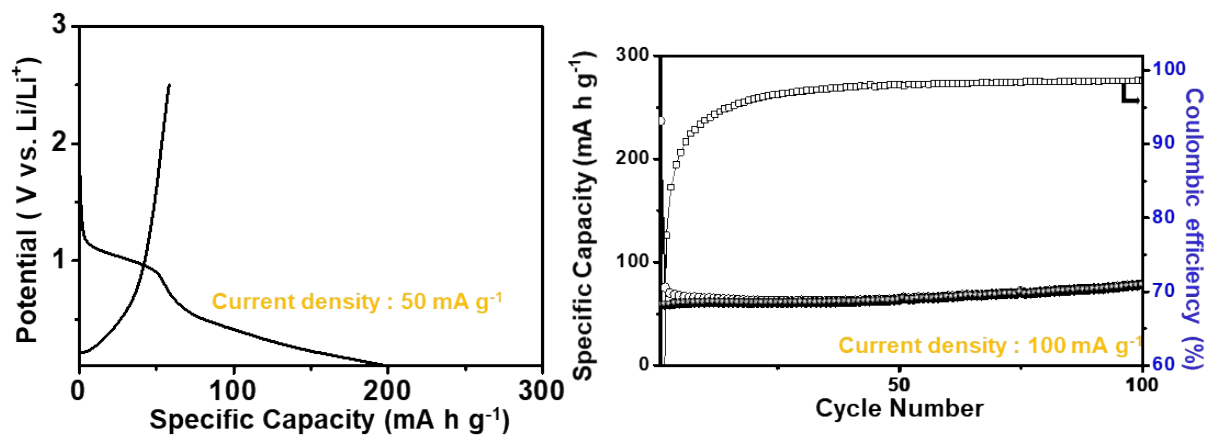


Fig. S14 Voltage profiles and cycle performance of acetylene carbon black electrode for SIBs at current densities of 50 and 100 mA g⁻¹, respectively.

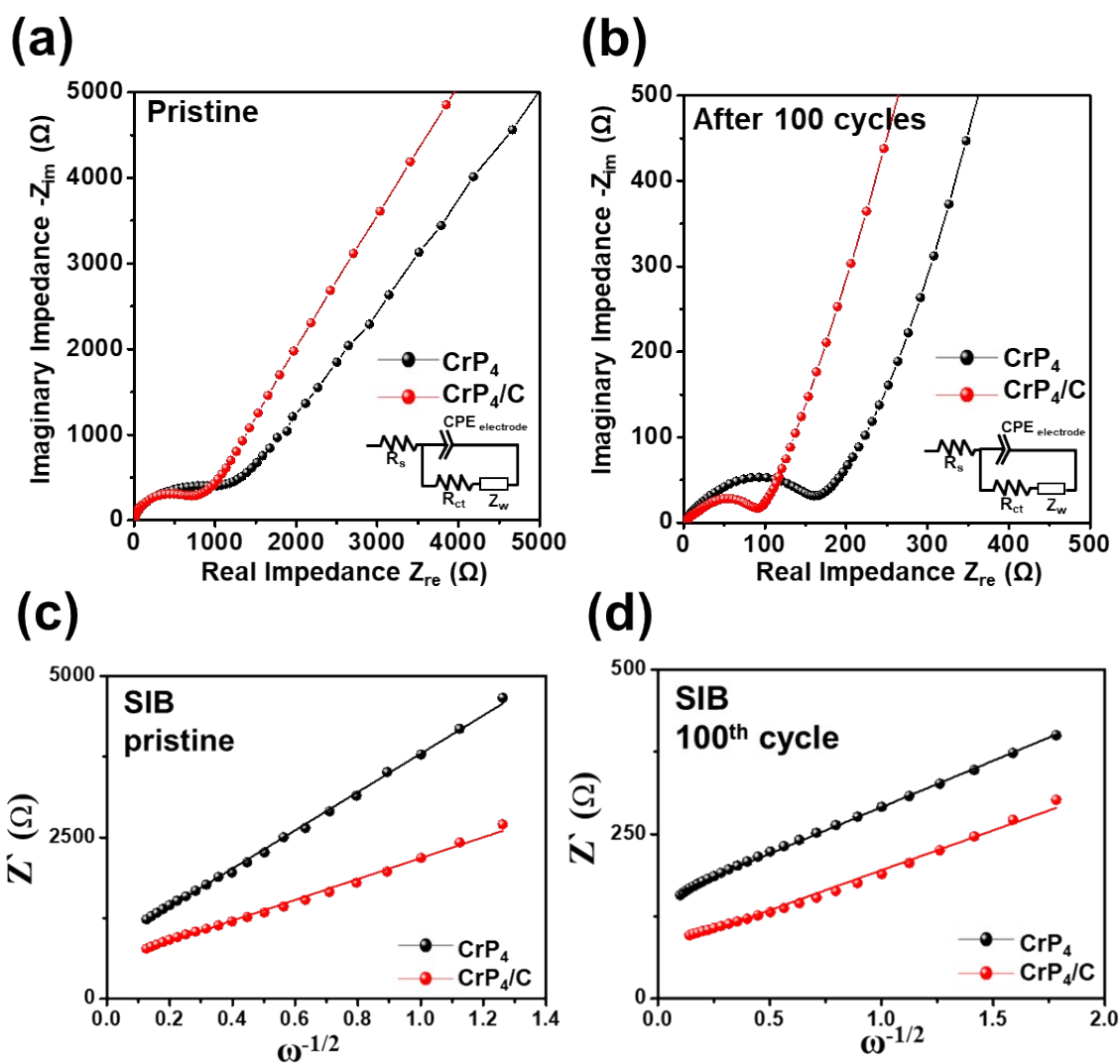


Fig. S15 Fitted Nyquist plots of CrP_4 and CrP_4/C electrodes (a) at pristine and (b) after 100 cycles and relationship between Z' and $\omega^{-1/2}$ (c) at pristine and (d) after 100 cycles at a current density of 500 mA g^{-1} in SIBs.

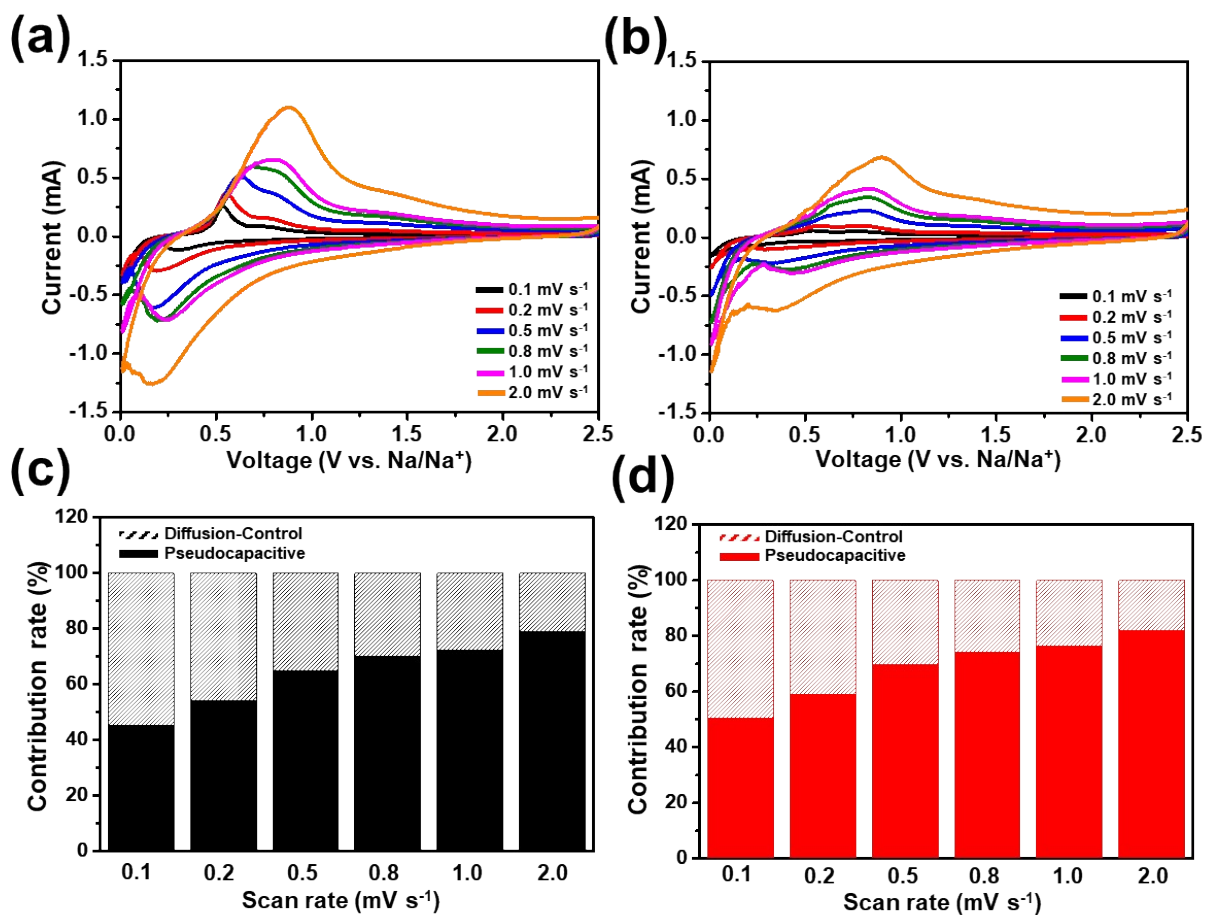


Fig. S16 CV curves and corresponding normalized contribution ratios of diffusion-controlled and pseudocapacitive-controlled at various scan rates from 0.1-2.0 mV s⁻¹ of (a, c) CrP₄ and (b, d) CrP₄/C electrodes in SIBs, respectively.

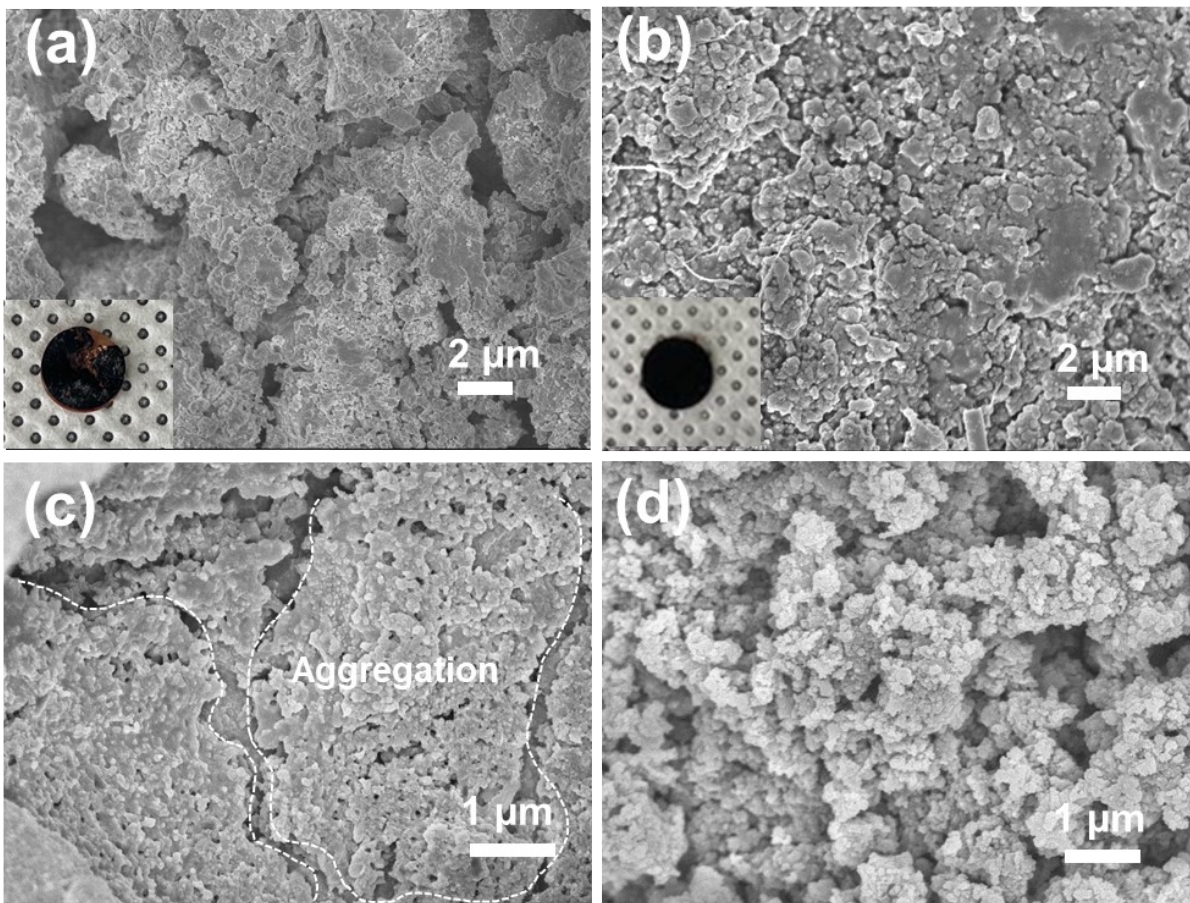


Fig. S17 SEM images of the electrodes before and after rinsing SEI layer of (a, c) CrP₄ and (b, d) CrP₄/C electrodes, respectively, after 100 cycles at a current density of 500 mA g⁻¹ in SIBs (inset in (a) and (b): optical images of each electrodes).

Table S1 Le Bail fitting result of as-synthesized CrP₄ nanoparticles.

| | (Fitting result) | (ICDD #01-071-0547) |
|--------------------------|-------------------|---------------------|
| Crystal structure | Monoclinic | Monoclinic |
| Space group | C 2/c | C 2/c |
| a | 5.2002 Å | 5.1914 Å |
| b | 10.7258 Å | 10.7600 Å |
| c | 5.8042 Å | 5.7712 Å |
| α | 90° | 90° |
| β | 110.773° | 110.648° |
| γ | 90° | 90° |

Table S2 The fitted charge transfer resistance (R_{ct}) and ionic diffusion coefficient of CrP_4 and

| | CrP_4 | | CrP_4/C | |
|----------------------------|----------------------------------|--|---|--|
| | R_{ct} (Ω) | D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$) | R_{ct} (Ω) | D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$) |
| Pristine | 626 | 8.56×10^{-15} | 558.7 | 1.06×10^{-14} |
| | R_{ct} (Ω) | D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$) | R_{ct} (Ω) | D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$) |
| After 50 cycles | 49.3 | 3.52×10^{-11} | 26.4 | 4.08×10^{-11} |

CrP_4/C electrodes in LIBs.

Table S3 The fitted charge transfer resistance (R_{ct}) and ionic diffusion coefficient of CrP_4 and CrP_4/C electrodes in SIBs.

| | CrP_4 | | CrP_4/C | |
|-----------------------------|----------------------------------|--|---|--|
| | R_{ct} (Ω) | D_{Na^+} ($\text{cm}^2 \text{ s}^{-1}$) | R_{ct} (Ω) | D_{Na^+} ($\text{cm}^2 \text{ s}^{-1}$) |
| Pristine | 1265 | 6.52×10^{-15} | 825.3 | 2.20×10^{-14} |
| | R_{ct} (Ω) | D_{Na^+} ($\text{cm}^2 \text{ s}^{-1}$) | R_{ct} (Ω) | D_{Na^+} ($\text{cm}^2 \text{ s}^{-1}$) |
| After 100 cycles | 130.3 | 2.85×10^{-12} | 98.5 | 3.91×10^{-12} |