

**Insights into Electrolyte-Dependent Interfacial Chemistry in High-voltage
Na₃VFe(PO₄)₃ Cathode through Combined Experimental and Theoretical Studies**

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To investigate Na⁺ diffusion kinetics, EIS measurements were performed in the frequency range from 0.01 to 100 kHz. The Na⁺ diffusion coefficient (D_{Na^+}) is quantified by the following equations:¹

$$Z' = R_s + R_{ct} + R_{SEI} + \sigma \cdot \omega^{-1/2} \quad (S1)$$

$$D_{Na^+} = 0.5 \left(\frac{RT}{An^2F^2\sigma C} \right)^2 \quad (S2)$$

Where ω is the angular frequency, and σ is the Warburg factor. σ can be determined by the slope of $\sim\omega^{-1/2}$ vs Z' plots. R, T, A, n, F and C are gas constant, test temperature, electrode surface area, number of electrons transferred, Faraday constant, and the concentration of Na⁺, respectively. The values can be compared qualitatively through the D_{Na^+} and σ values.

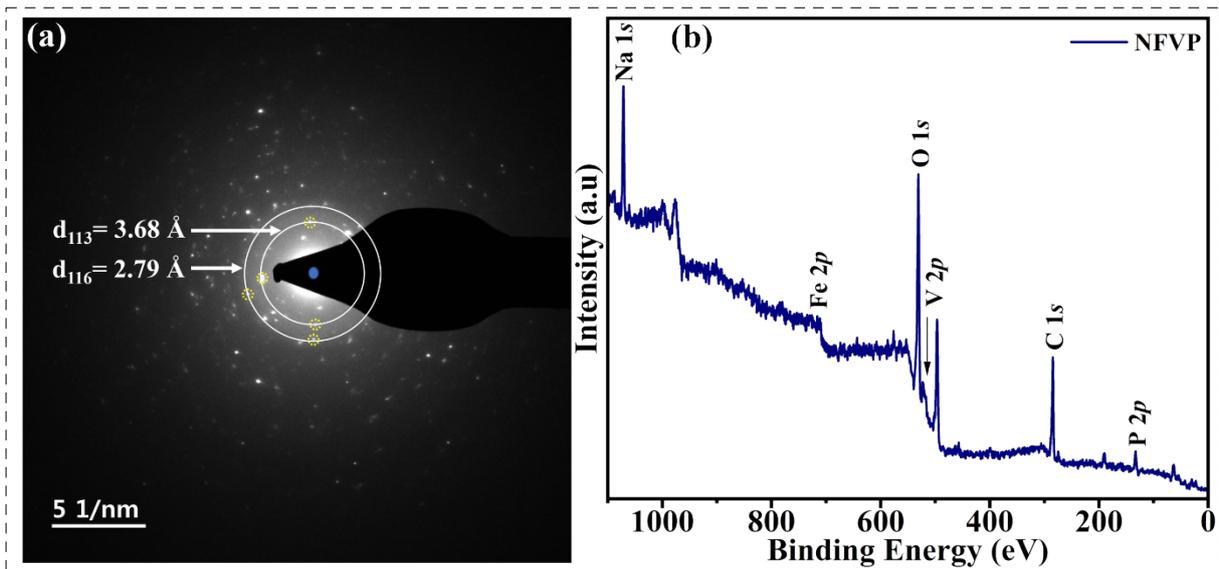


Figure S1. (a) SAED pattern, and (b) survey scan of NVFP.

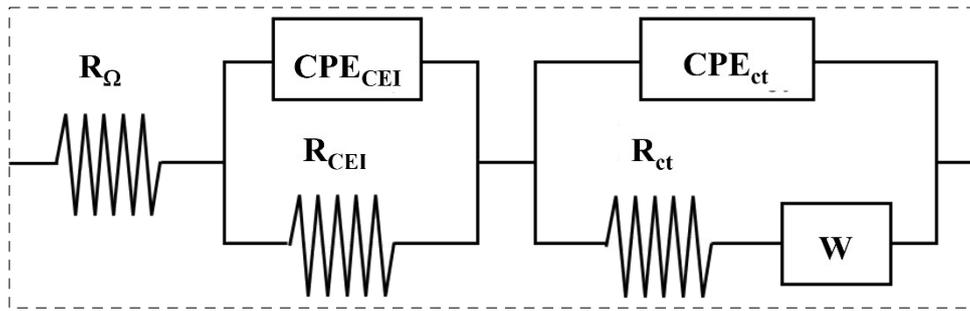


Figure S2. An equivalent electrochemical circuit used for fitting Nyquist plots of NVFP1.

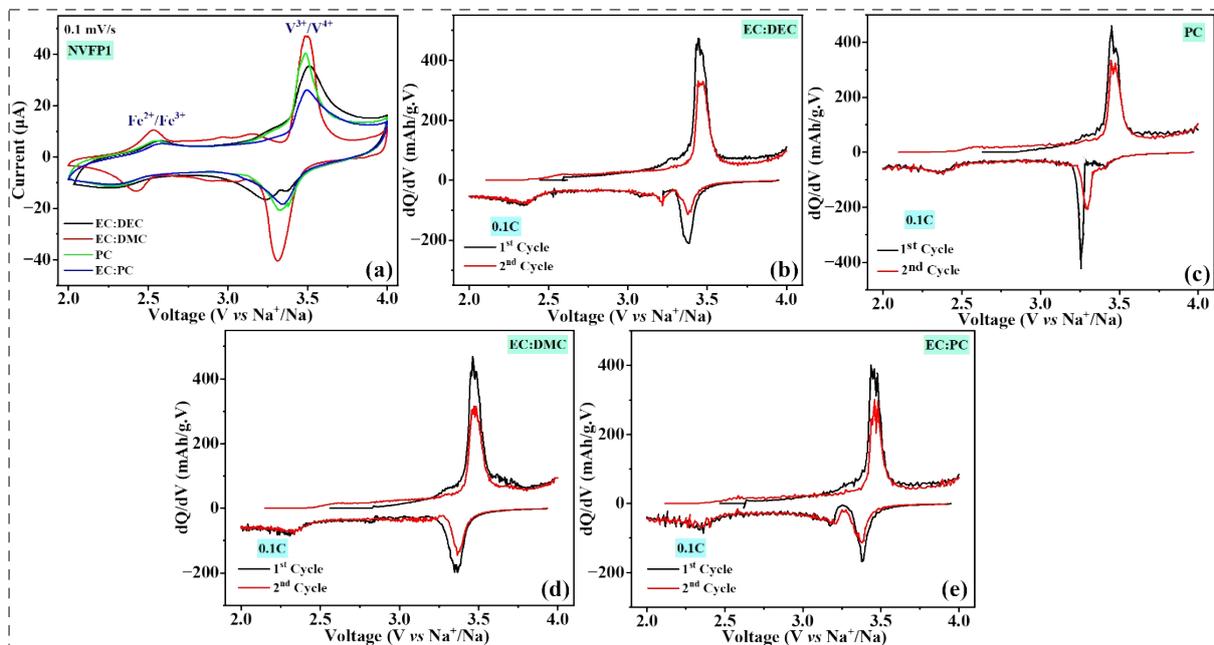


Figure S3. (a) CV of NVFP1 in all electrolyte systems at 0.1 mV/s, differential CV of NVFP1 in (b) EC:DEC, (c) PC, (d) EC:DMC, and (e) EC:PC electrolyte systems at 0.1C.



Figure S4. The structure of the NVFP crystal indicates two distinct possible Na sites: Na1 and Na2.

Table S1. Comparison of the electrochemical performance of the present study with previously reported materials and their derivatives

Composition	Voltage Window (V)	Average Operating Voltage (V vs Na ⁺ /Na)	Specific Dis. Capacity (mAh/g) @C rate	Retention, Cycle Number@C rate	Ref.
Na ₃ VFe(PO ₄) ₃	~ 3.2	1.8-3.9	105@0.1C	87.6 %, 400@5C	2
Na ₃ VFe(PO ₄) ₃	~ 3.4	2.2-3.8	103@1C	95%, 2000@1C	3
Na ₃ VCr(PO ₄) ₃	~ 3.4	2.5-4.3	90@0.1C	-	4
Na ₃ VMn _{0.5} Ti _{0.5} (PO ₄) ₃ /C	~ 3.4	1.5-4.15	144.3@0.13C	88.13%, 500@0.85C	5
Na ₃ VFe _{0.5} Ti _{0.5} (PO ₄) ₃ /C	~ 3.4	1.5-4.15	145@ 0.12C	92%, 6000@11.2C	6
Na₃VFe(PO₄)₃	~ 3.3	2.0-4.3	108.43@0.1C	86.11%, 2000@3C	This Work

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