

Dual-Ion Pre-Intercalated Vanadium Oxides Derived from V_4AlC_3 MAX via HF-Free Synthesis for Aqueous Zinc-Ion Batteries

Lejun Li,^a Zengrong Mao,^a Wenhai Xiao,^a Junling Xu,^a Xiaoyan Shi,^a Lianyi Shao,^{*a} Zhipeng Sun,^{*a} Chengcheng Chen,^{*c} Lifeng Hang^{*b}

^aSchool of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, Guangdong, China. E-mail: shaolianyi@gdut.edu.cn, zpsunxj@gdut.edu.cn

^bDepartment of Medical Imaging, The Affiliated Guangdong Second Provincial General Hospital of Jinan University, Guangzhou, Guangdong, 518037, China. E-mail: hanglf@ustc.edu.cn

^cChina Electronic Product Reliability and Environmental Testing Research Institute (CEPREI), Guangzhou, Guangdong 511370, China. Email: chenchengcheng@ceprei.com

Experimental Section

Material characterization

The phase composition of the CaAlVO material was analyzed using X-ray diffraction (XRD) with a Rigaku D/Max-III diffractometer, equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the CaAlVO composite was examined using a field emission scanning electron microscope (SEM, HITACHI SU8010). Raman spectra were obtained using a micro-Raman spectrometer (Renishaw inVia Qontor) with a 532 nm laser for excitation. X-ray photoelectron spectroscopy (XPS) was conducted using a K-Alpha X-ray photoelectron spectroscopy system, employing a monochromatic Al K α source to analyze the chemical states of the materials. Transmission electron microscopy (TEM) images were captured using a FEL Tecnai F30 device. This instrument also facilitated the analysis of elemental distribution and chemical composition through energy-dispersive X-ray spectroscopy (EDS).

Electrochemical Characterization

The working electrodes were fabricated by mixing CaAlVO with superconducting carbon black and polyvinylidene fluoride (PVDF) at a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP). The obtained slurry was evenly coated on a stainless steel mesh and then vacuum dried at 60 °C for 12 h. The active material in the electrode for

the coin battery was 1.5–3 mg cm⁻². Using 3M Zn(CF₃SO₃)₂ aqueous solution as the electrolyte, glass fiber as a separator, and metal zinc as a negative electrode, the coin/soft packaging batteries were assembled in the air. The mass of active material in the soft packaging battery was around 0.9–1.6 mg cm⁻². The soft packaging batteries were assembled using aluminum-plastic film as the outer packaging, containing CaAlVO-2 cathode (3×3 cm², 14.595 mg) and Zn(CF₃SO₃)₂ electrolyte (1.5 mL). The electrochemical performance of these batteries was tested using the Neware battery testing system (CT4008T) at 0.2–1.6 V. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using Chenhua electrochemical workstation (CHI660E).

The galvanostatic intermittent titration technique (GITT) was employed to measure the Zn²⁺ diffusion coefficient ($D_{\text{Zn}^{2+}}$) within a charge/discharge time of 10 mins and followed by a relaxation time of 30 mins at 0.1 A g⁻¹. The assembled ZIBs were first discharged and charged in two cycles at 0.1 A g⁻¹ to reach a stable state. Then the GITT measurements were performed. $D_{\text{Zn}^{2+}}$ was calculated according to the following formula:

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2$$

where m_B , M_B , and V_M refer to the mass loading (g), molar mass (g mol⁻¹), and molar volume (cm⁻³ mol⁻¹) for CaAlVO, τ is current pulse time (s), ΔE_τ refers to the IR-drop-corrected voltage variation (V) during the constant-current pulse, while ΔE_s denotes the steady-state potential change (V) resulting from this pulse.

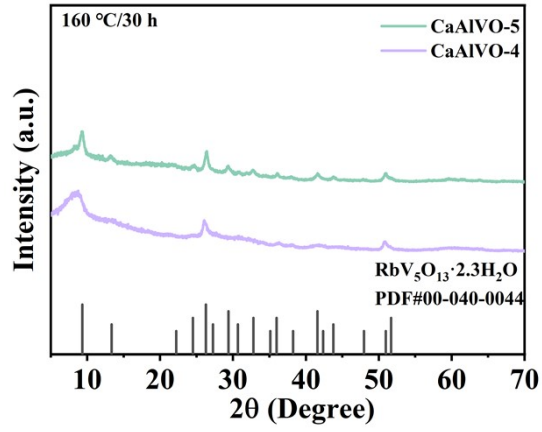


Figure S1. XRD patterns of CaAlVO synthesized at different acid-base ratios.

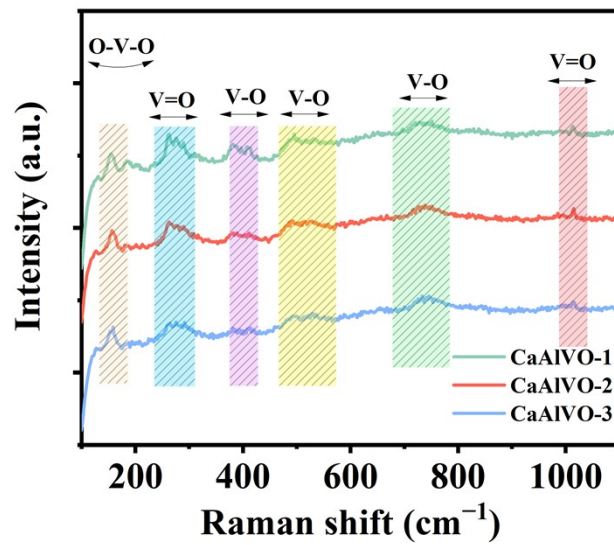


Figure S2. Raman curves of CaAlVO.

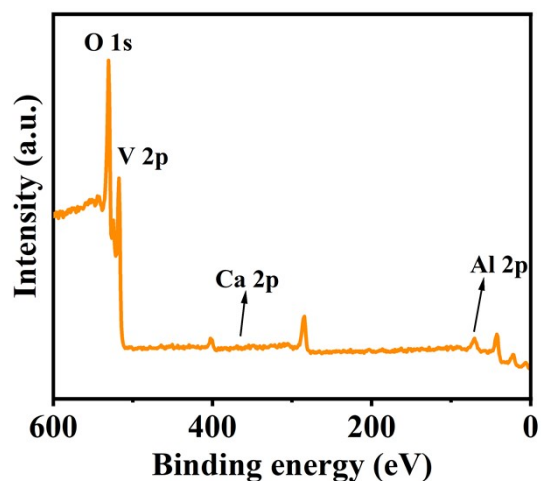
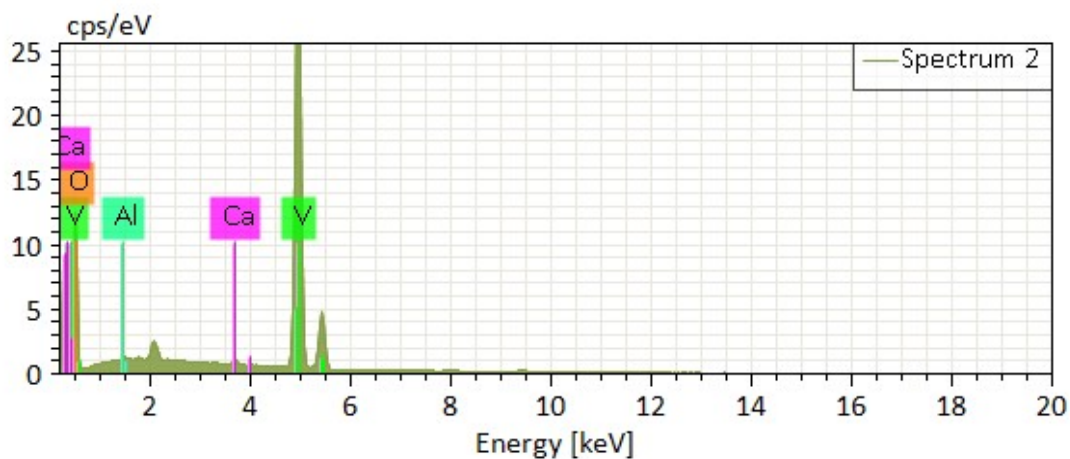


Figure S3. XPS survey spectrum of CaAlVO-2.



Element	Normalized data (%)	Atom (%)	Abs.error (%)
O	37.12	65.22	3.09
Al	0.08	0.08	0.02
Ca	0.35	0.25	0.02
V	62.45	34.46	1.58
	100	100	

Figure S4. EDS reports of CaAlVO-1.

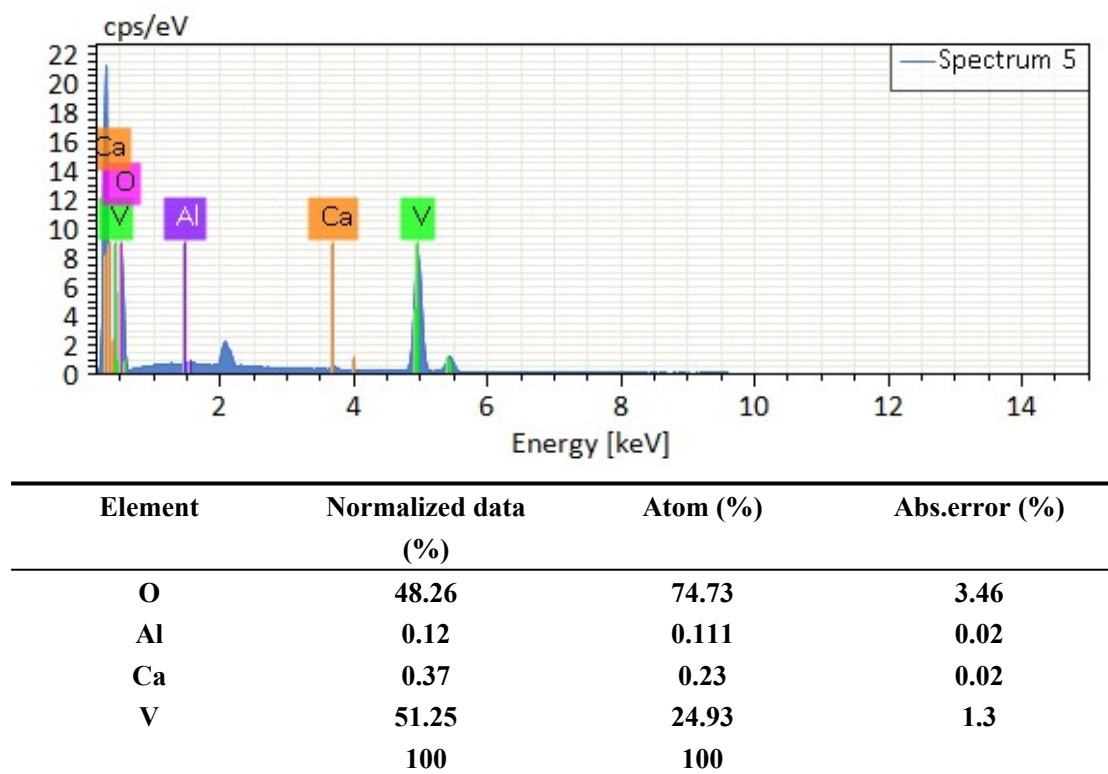


Figure S5. EDS reports of CaAlVO-2.

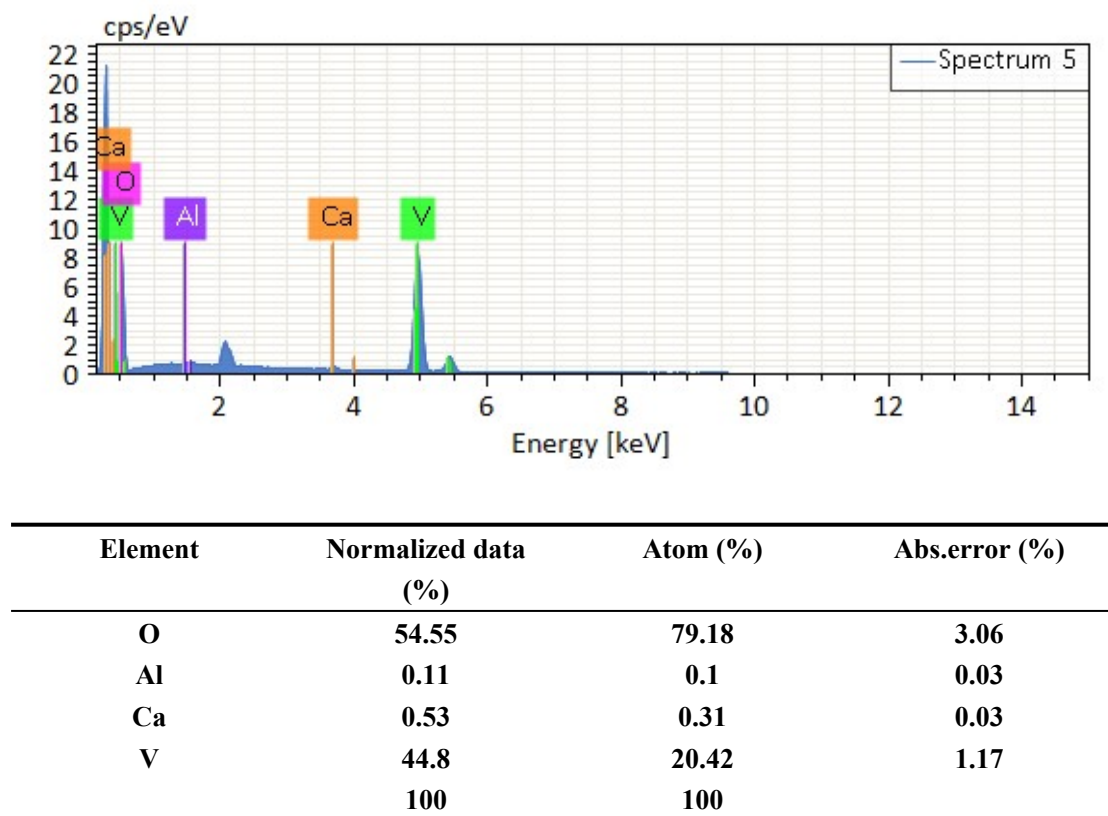


Figure S6. EDS reports of CaAlVO-3.

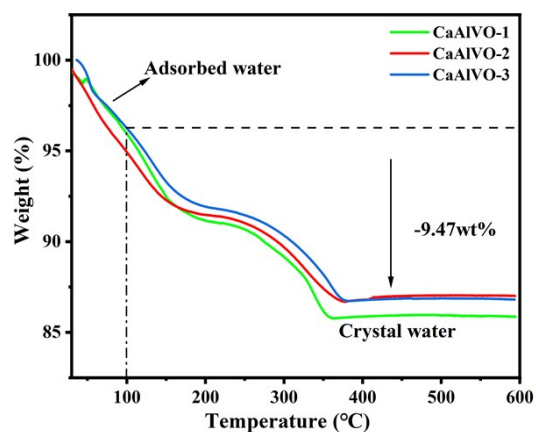


Figure S7. TGA curves of CaAlVO-1, CaAlVO-2, and CaAlVO-3.

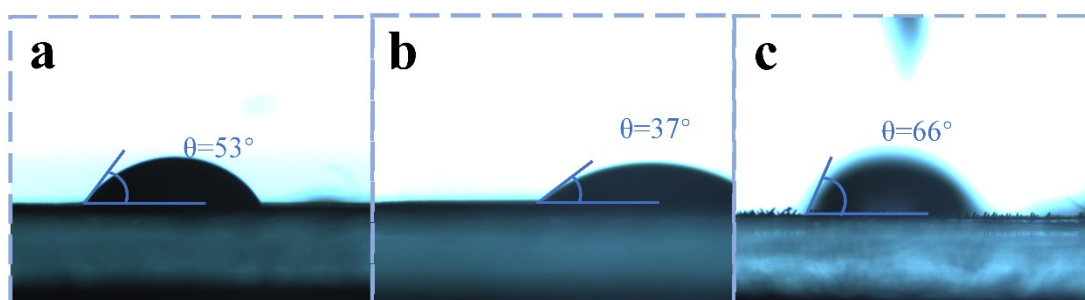


Figure S8. Contact angles of CaAlVO-1, CaAlVO-2, and CaAlVO-3.

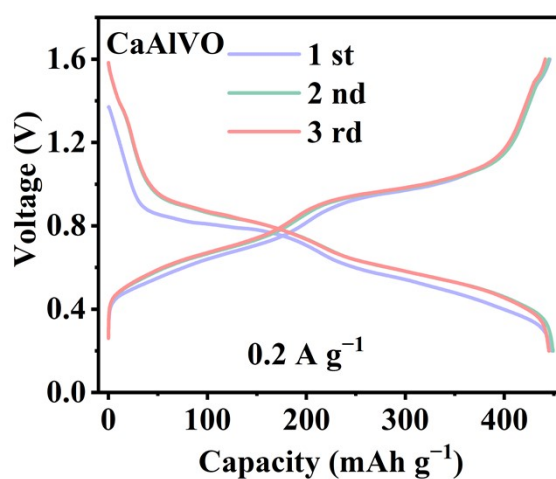


Figure S9. Initial three charge/discharge curves for CaAlVO-2 at 0.2 A g^{-1} .

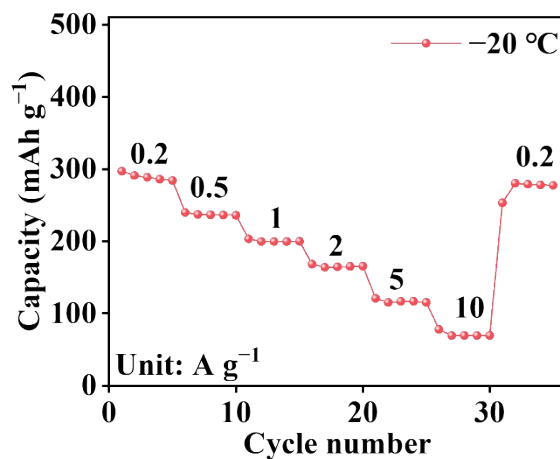


Figure S10. Rate performance of CaAlVO-2 at $-20\text{ }^{\circ}\text{C}$.

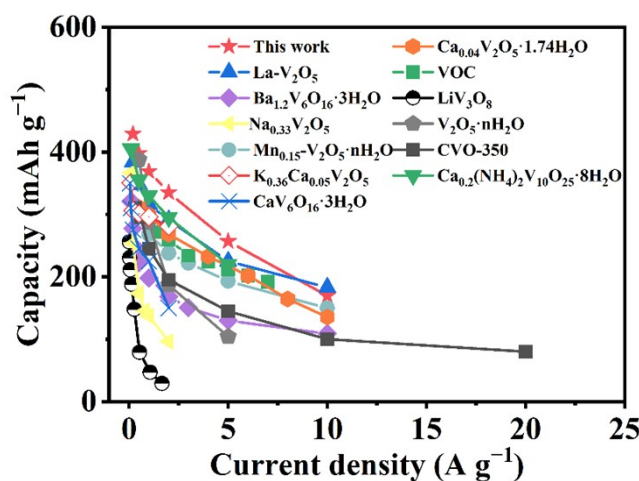


Figure S11. Comparison of rate performance with other vanadium oxides.

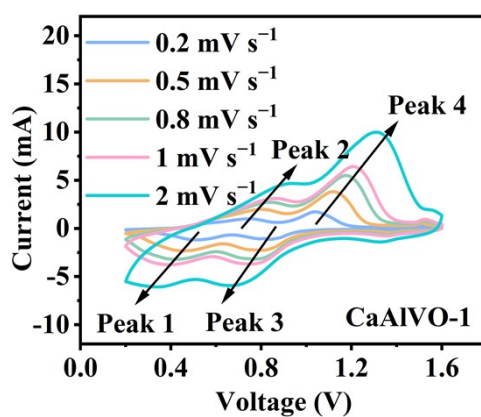


Figure S12. CV curves of CaAlVO-1.

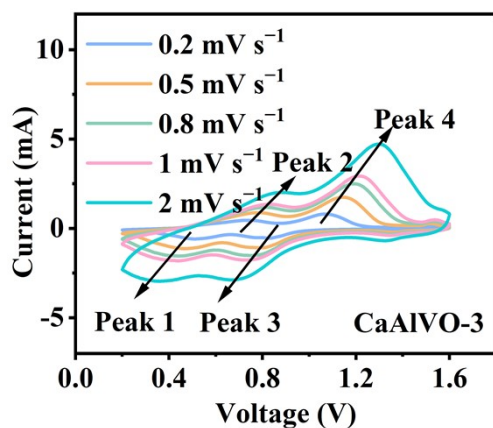


Figure S13. CV curves of CaAlVO-3.

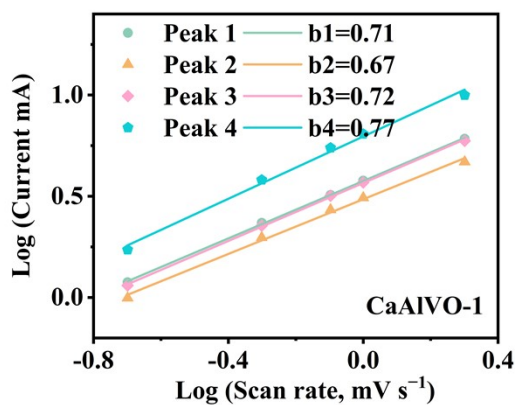


Figure S14. The b value plots of CaAlVO-1.

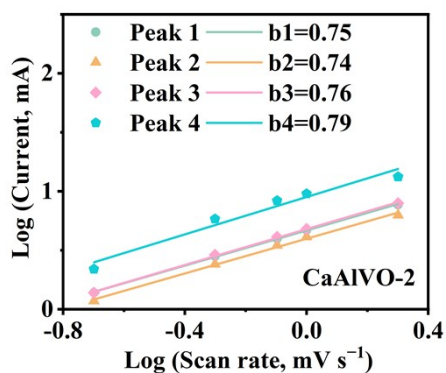


Figure S15. The b value plots of CaAlVO-2.

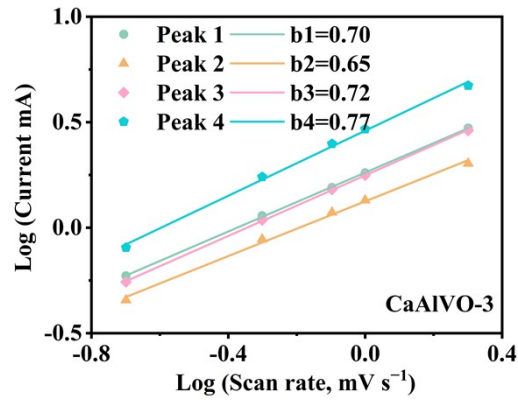


Figure S16. The b value plots of CaAlVO-3.

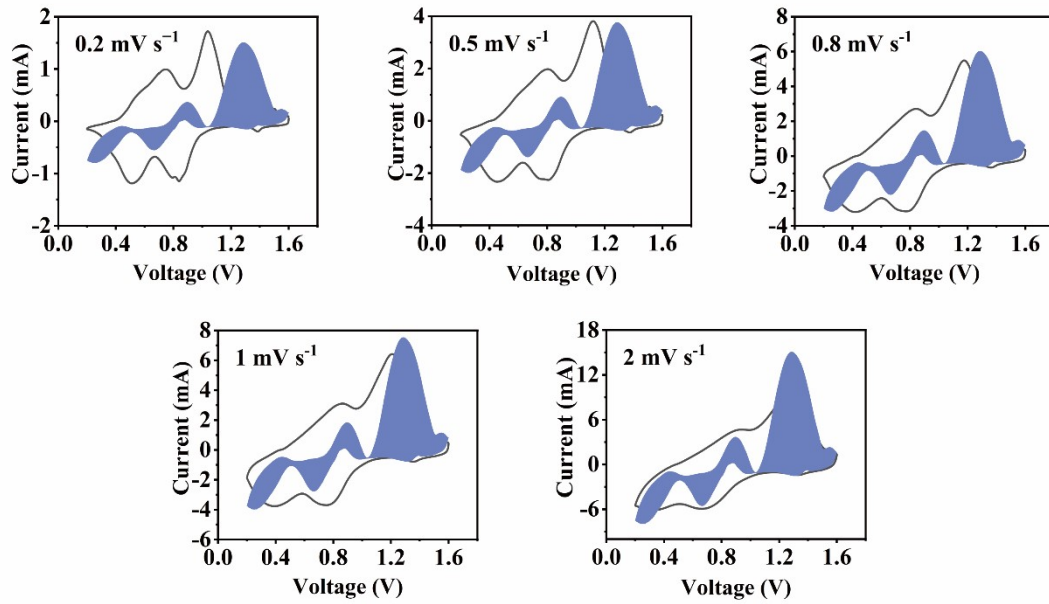


Figure S17. Capacitive controlled portion of CaAlVO-1 at different scan rates.

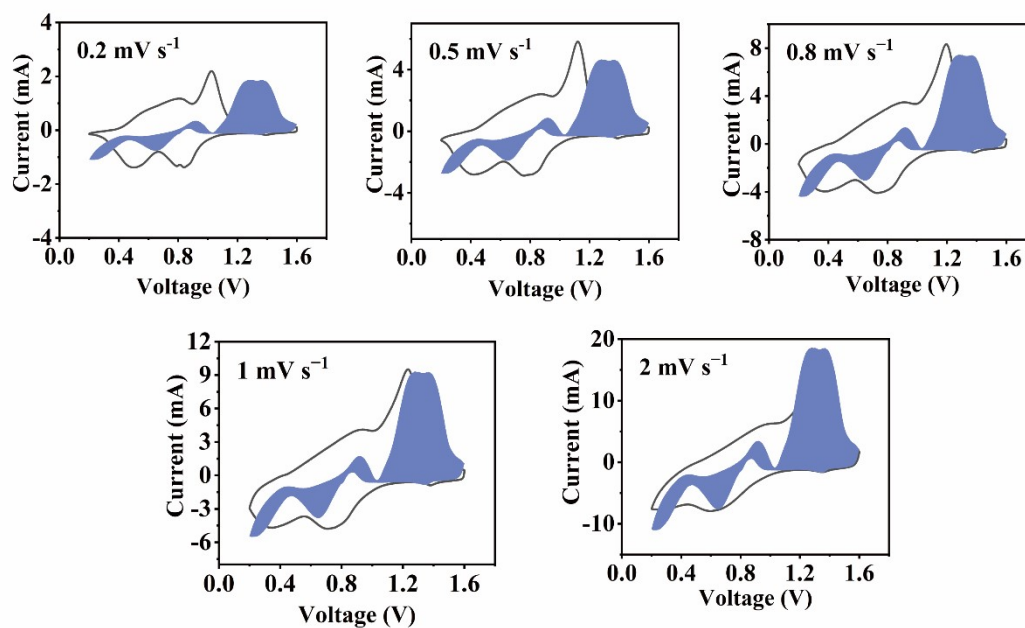


Figure S18. Capacitive controlled portion of CaAlVO-2 at different scan rates.

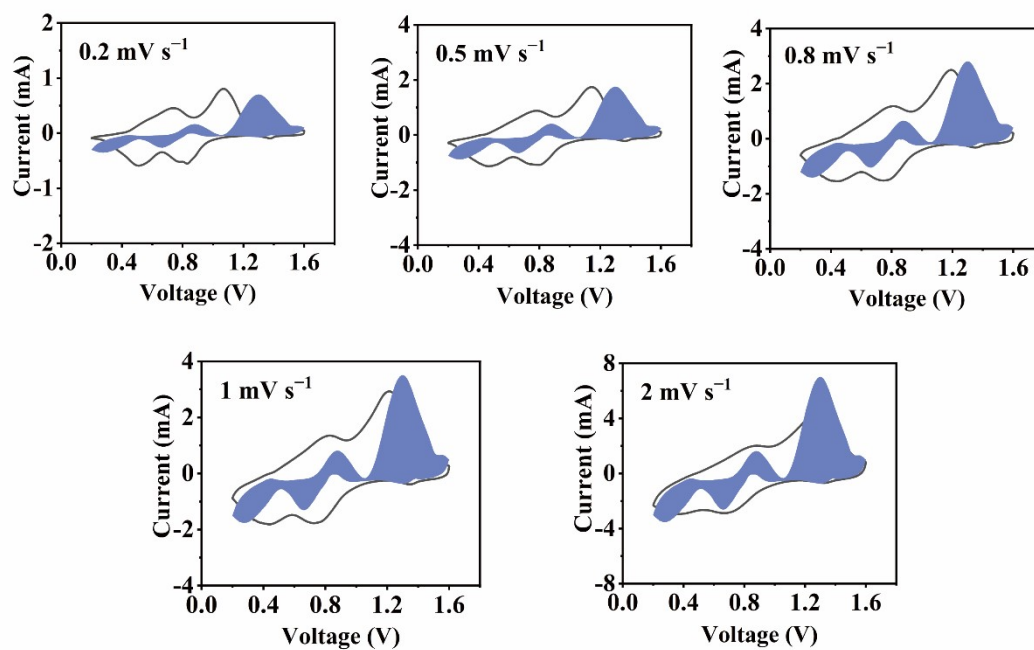


Figure S19. Capacitive controlled portion of CaAlVO-3 at different scan rates.

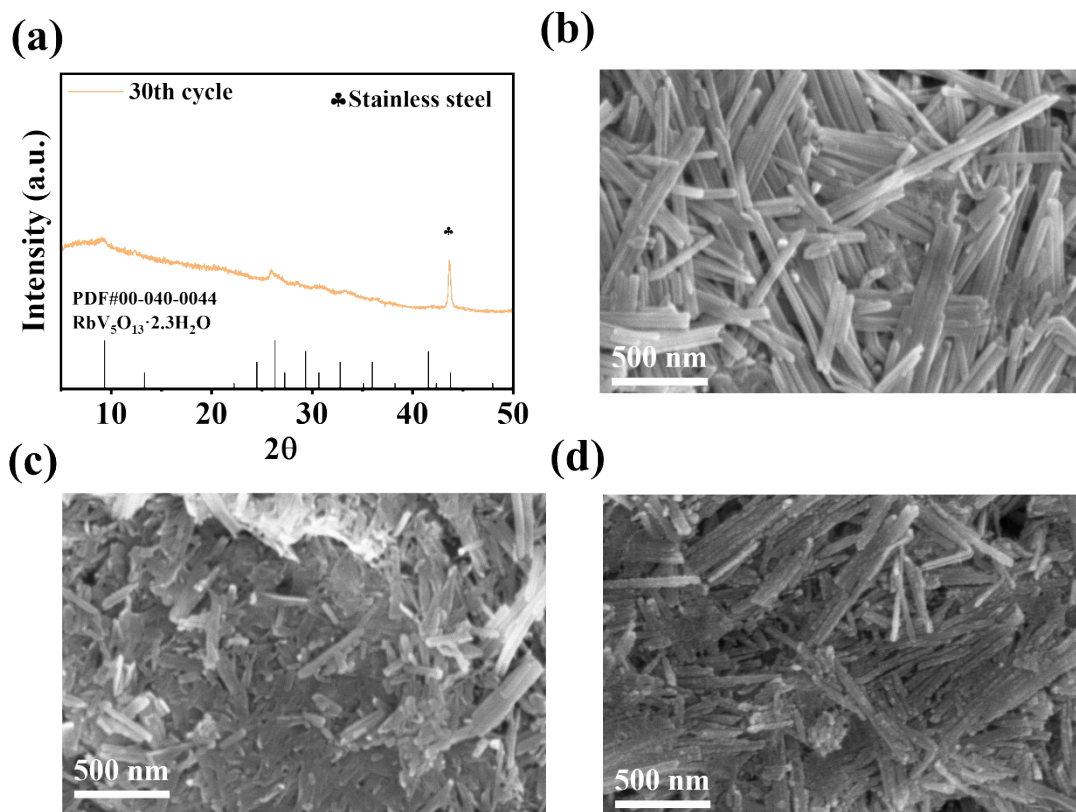


Figure S20. (a) XRD pattern of CaAlVO-2 electrode after 30 cycles at 0.2 A g⁻¹. SEM images of CaAlVO-2 (b) after initial cycle, (c) after 10 cycles, (d) after 50 cycles.

Table S1. Property comparison of the preintercalated M cations.

M cation	Al	Ca
Ionic radius (Å)	0.53	1
Hydrated ion Radis (Å)	4.8	4
Electronegativity of element	1.61	1
Electronegativity difference with O (3.44)	1.83	2.44