

Supplementary Information

Layered Iron Vanadate as a High-Capacity Cathode Material for Nonaqueous Calcium-Ion Batteries

Munseok S. Chae¹, Dedy Setiawan¹, Hyojeong J. Kim¹, and Seung-Tae Hong^{1,2,*}

¹ Department of Energy Science and Engineering, DGIST (Daegu Gyeongbuk Institute of Science and Technology), Daegu 42988, Republic of Korea

² Energy Science and Engineering Research Center, DGIST, Daegu 42988, Republic of Korea

*e-mail: st.hong@dgist.ac.kr

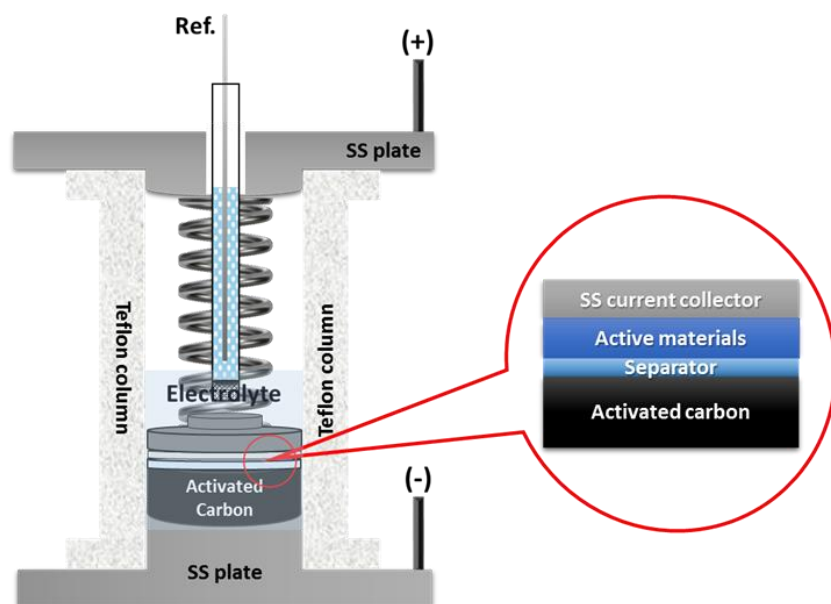


Figure S1. Scheme of the homemade cell used for electrochemical characterizations.

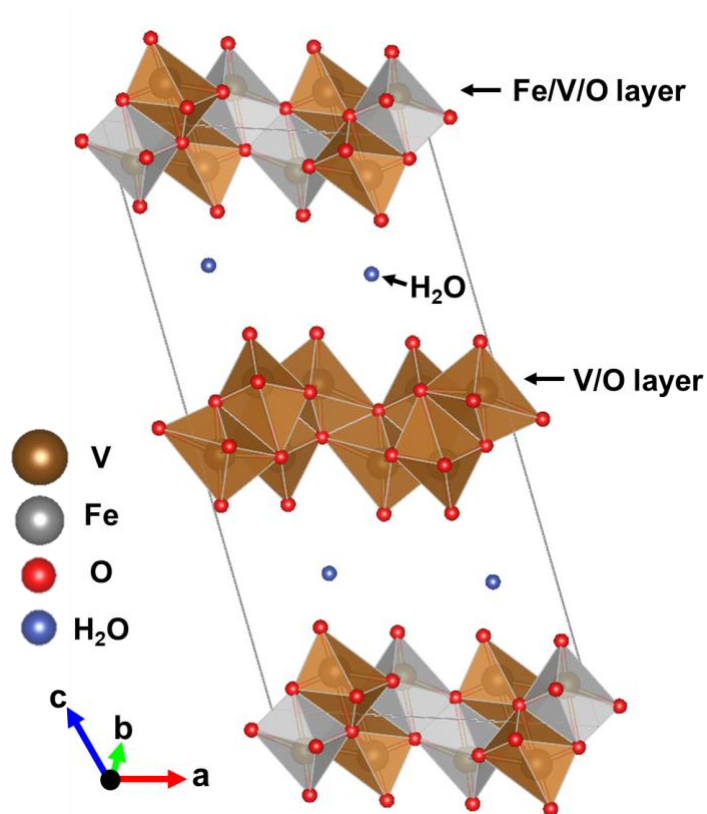


Figure S2. A proposed crystal structural model for $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$.

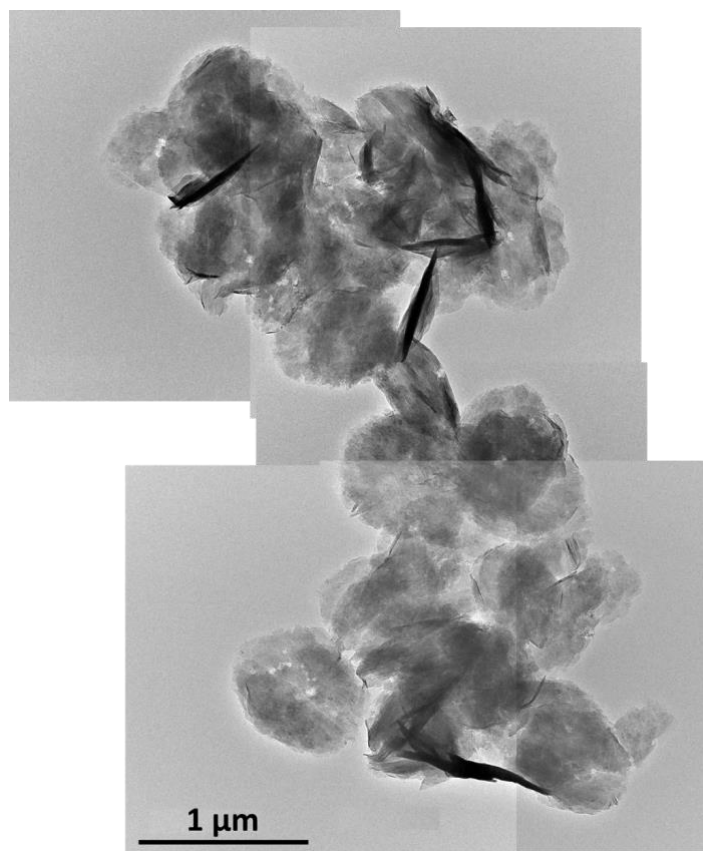


Figure S3. TEM images of the synthesized $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$ particles.

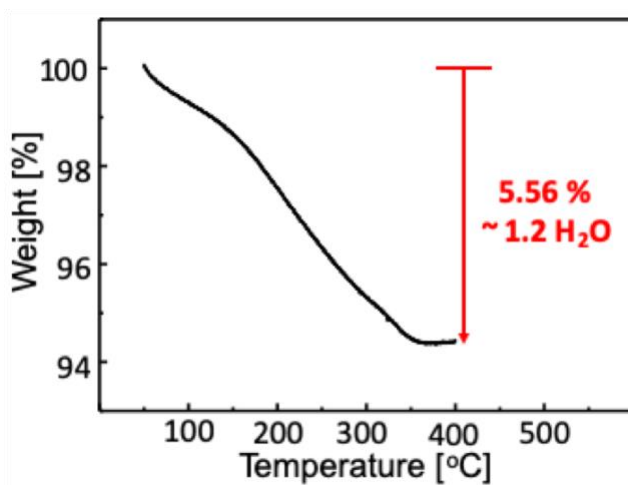


Figure S4. Thermogravimetric analysis for pristine $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$ sample under nitrogen flowing atmosphere.

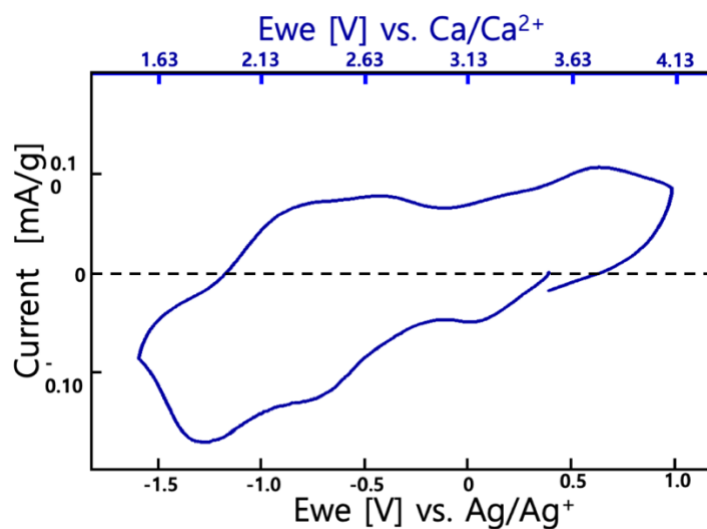


Figure S5. CV of $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$ electrode at 0.2 mV s^{-1} in $0.5 \text{ M Ca}(\text{ClO}_4)_2$ in AN with Ag/Ag^+ reference electrode in a three-electrode system.

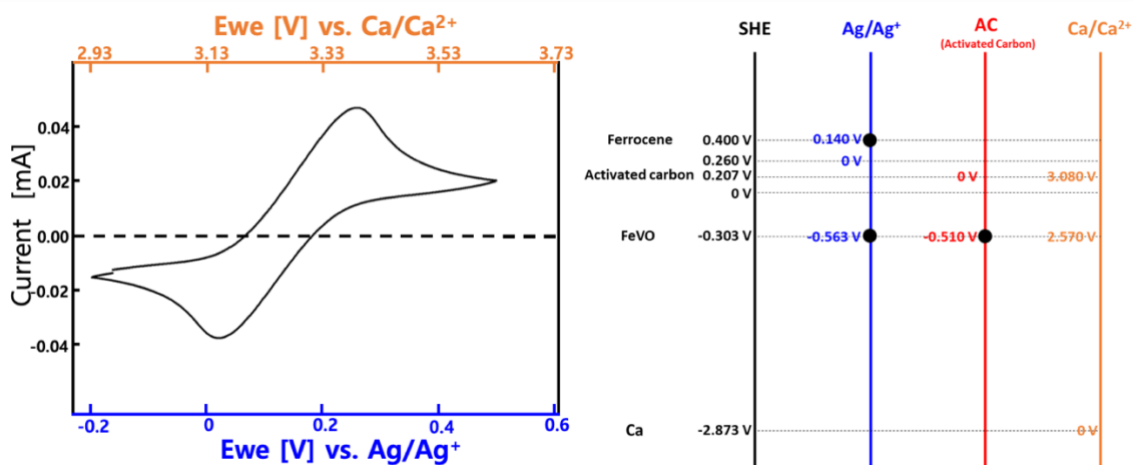


Figure S6. Ferrocene/ferrocenium redox couple CV test to estimate the AC voltage vs Ca/Ca^{2+} .

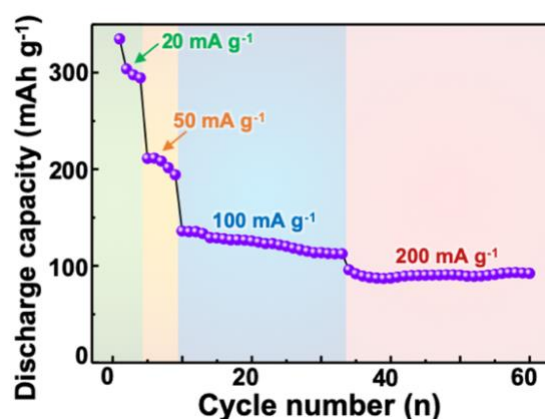


Figure S7. Cycle performance with various C-rates.

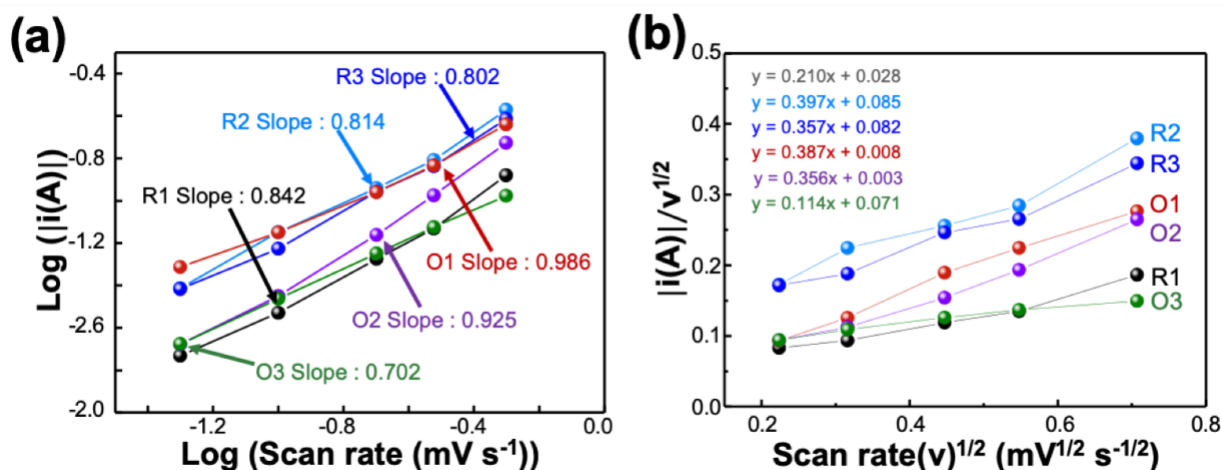


Figure S8. (a) Log–log plot of cathodic/anodic peak current dependence on the scan rate. (b) Plot of peak current ($i/v^{1/2}$) dependence on the square root of scan rate ($\text{mV}^{1/2} \text{ s}^{-1/2}$). According to Power's law,[1] the scan rate dependence of the CV current can be expressed as the equation:[1,2]: $i = av^b$, where i is the current (measured in A), v is the scan rate (mV s^{-1}), and a and b are the adjustable parameters. The b -value can be determined by the slope of the $\log(v)$ versus $\log(i)$ plots, and generally between 0.5–1.0 (a). The estimated b -value is 0.5 for an ideal diffusion-controlled Faradaic intercalation reaction, 1.0 for a non-Faradaic capacitive process, and an intermediate value suggests a combined charge-storage reaction mechanism. Quantification of each contribution can be estimated using the method proposed by Dunn et al.,[1] from the linear plot of $i(V) v^{-1/2}$ vs. $v^{1/2}$ (b). For each of the scan rates, the intercalation and adsorption contributions were calculated. Figure 2e is the contribution ratio for the R2 peak current, for example.

1. Wang, J.; Polleux, J.; Lim, J.; Dunn, B. Pseudocapacitive contributions to electrochemical energy storage in TiO_2 (anatase) nanoparticles. *J. Phys. Chem. C* **2007**, *111*, 14925–14931.
2. Yin, H.; Song, C.; Wang, Y.; Li, S.; Zeng, M.; Zhang, Z.; Zhu, Z.; Yu, K. Influence of morphologies and pseudocapacitive contributions for charge storage in V_2O_5 micro/nano-structures. *Electrochim. Acta* **2013**, *111*, 762–770.

Table S1. Elemental ratios estimated from ICP analysis for $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$ sample.

	Mass ratio (%)			Relative atomic ratio		
	Ca	Fe	V	Ca	Fe	V
Sample						
Pristine $\text{FeV}_3\text{O}_9 \cdot 1.2(\text{H}_2\text{O})$	0.00	26.6	73.4	0.0	5.0	15.0

Table S2. Elemental ratios estimated from ICP analysis for the pristine $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$, first discharged, and first charged electrodes.

	Mass ratio (%)			Relative atomic ratio		
	Ca	Fe	V	Ca	Fe	V
Sample						
Pristine $\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$	0.0	26.6	73.4	0.0	5.0	15
Discharged $\text{Ca}_{1.9}\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$	26.5	19.5	54.0	1.9	5.0	15
Charged $\text{Ca}_{0.2}\text{FeV}_3\text{O}_9 \cdot 1.2\text{H}_2\text{O}$	3.64	25.8	70.5	0.2	5.0	15