Supporting Information

Calcium Molybdenum Bronze as a Stable High-Capacity Cathode Material for Calcium-Ion Batteries

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1. Experimental Section

Synthesis and materials characterization:

Calcium molybdenum bronze, Ca_{0.13}MoO₃·(H₂O)_{0.41} (CMO) was prepared using a chemical cation exchange method from Na_{0.25}MoO₃·(H₂O)_{0.49},¹ which was synthesized via a chemical reduction from α-MoO₃ in the Na₂MoO₄·2(H₂O) and Na₂S₂O₄ mixed solution at room temperature in argon filled atmosphere.² The MoO₃ (4 g, \geq 99.5%, Alfa Aesar) powder were suspended in the 200 ml of deionized water with vigorous stirring and argon gas bubbling for one hour at room temperature. Then, the powder mixture of 1.6 g Na₂S₂O₄ (\geq 99.5%, Sigma Aldrich) and 48 g Na₂MoO₄·2(H₂O) (\geq 99.5%, Sigma Aldrich) was added into the MoO₃ suspension. The mixture was reacted for three hours with vigorous stirring and argon bubbling at room temperature. The dark blue product was collected by filtration with aspiration, carefully washed with deionized water, and finally dried at 50 °C for 24 h in air. Then, the Na_{0.25}MoO₃·(H₂O)_{0.49} powder was redispersed in 100 ml of 1 M CaCl₂ aqueous solution for two days, to exchange sodium to calcium ions. Finally, the synthesized CMO powder was collected by filtration with careful washing with deionized water, then dried at 50 °C for 24 h in air. The morphological and elemental analyses were performed using ICP-OES analysis (Varian 700-ES), field-emission transmission electron microscopy (FE-TEM, Hitachi HF-3300), and field-emission scanning electron microscopy (FE-SEM, Hitachi SU-8020) with an EDX attachment. The water content of the electrode materials was obtained by thermogravimetric (TG) analysis (Rigaku TG 8120).

Electrochemical characterization:

For the electrochemical measurements, the home-made cell was used for all electrochemical experiments (Figure S4), with the EC-Lab software on a Biologic VMP3 multichannel potentiostat (Biologic Science Instruments SAS). The working electrode consists of the synthesized CMO powder, Super P carbon black (Timcal Graphite & Carbon), and composite binder of carboxymethyl cellulose (CMC, LG Chem.) and styrene butadiene rubber (SBR, LG Chem) (80:15:4:1 w/w), which were mixed and dispersed in deionized water, and coated on 20 μ m stainless steel foil (SUS-316L), dried overnight at 60 °C in an oven to remove the water, pressed by an electrode rolling press (Wellcos Co., Korea). The electrode area was 1.53 cm², with the loading of ~2.8 mg of CMO on each electrode. The activated carbon pellet (2530-1405, Daejung

Chemicals & Metals, Korea) was used as the counter and reference electrodes (approximately 0.8 g, thickness = 5 mm, φ = 1.8 mm), glass fiber (GF/A, Whatman) was used as a separator, and 0.5 M calcium perchlorate (Reagent grade, Alfa Aesar) in acetonitrile (99.8%, Samchun, Korea) was used as the organic electrolyte. The water content of the electrolyte was 27 ppm initially, and 38 ppm after the first charge, according to the water analysis (Metrohm, 831 KF coulometer). The calcium perchlorate was dried at 220 °C for three days,³ and the acetonitrile was treated with molecular sieves to remove the water before use.

The potential of the AC electrode was calculated as 3.063 V vs. Ca/Ca²⁺ by comparing the CV curves using the AC reference electrode with that using the Ag/Ag⁺ reference electrode; the Ag/Ag⁺ electrode voltage was calibrated with the ferrocene/ferrocenium redox couple (Figure S5 and S6)

Structural analysis:

The powder X-ray diffraction (XRD) were collected at 25 °C using an X-ray diffractometer (PANalytical Empyrean X-ray diffractometer) with Cu $K\alpha_1$ X-ray tube ($\lambda = 1.5406$ Å) with a Ge (111) monochromator, a position-sensitive PIXcel3D 2×2 detector, an angular range of $5^\circ \le 2\theta \le 150^\circ$, a step of 0.013000°, and a total measurement time of 10 h at room temperature. The crystal structure of Ca_{0.13}MoO₃·(H₂O)_{0.41} (CMO) and Ca_{0.50}MoO₃·(H₂O)_{0.37} (discharged CMO) was refined using the powder profile refinement program GSAS. The initial structural models of Ca_{0.13}MoO₃·(H₂O)_{0.41} were adopted from a previous report for sodium molybdenum bronze,² revised, and refined.

Bond Valence Sum Difference Map (BVS-DM) calculations:

The 3D bond-valence-sum difference-map (BVS-DM)⁴ calculations were performed with the code 3DBVSMAPPER,⁵ which was written in the Perl script language, within Materials Studio.⁶ The absolute values of the difference ($|\Delta v|$) between the calculated valence of Ca²⁺ in the CMO structure,¹ as an inserted state, were plotted as isosurfaces at each point on a 3D grid so that the plausible diffusion pathways could be graphically visualized.

REFERENCES

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2. Supporting figures and tables



Figure S1. Thermogravimetric analysis under nitrogen flowing atmosphere for (a) $Na_{0.25}MoO_3$ ·(H₂O)_{0.49}, and (b) the pristine CMO, first discharged, first recharged, and the 50th charged electrode samples. Note that the water content of CMO was nearly preserved during the cycles from the first discharged state, within experimental errors.



Figure S2. FE-SEM images of $Na_{0.25}MoO_3 \cdot (H_2O)_{0.49}$, as-synthesized CMO (x=0.13), and ballmilled CMO powder.



Figure S3. Powder X-ray Le Bail fitting for the pristine CMO sample of x=0.13, recorded at room temperature.



Figure S4. Scheme diagram of the fabricated home-made cell used for electrochemical characterizations.



Figure S5. CV of the CMO electrode at 0.1 mV s⁻¹ in a 0.5 M Ca(ClO₄)₂ in AN with Ag/Ag⁺ reference electrode in a three-electrode system.



Figure S6. Ferrocene test to estimate Ca/Ca^{2+} voltage, and the relationship between SHE (standard hydrogen electrode), Ag/Ag^+ , AC, and Ca/Ca^{2+} electrodes.



Figure S7. Initial galvanostatic discharge profiles for CMO with various C rates.



Figure S8. Cycle performance with various C rates.



Figure S9. (a) CV curves of CMO at various scan rates in 0.5 M Ca(ClO₄)₂/AN. (b) Log–log plot of cathodic peak current dependence on the scan rate to determine b-value for the insertion reaction. (c) The plot of cathodic peak current ($i/v^{1/2}$) dependence on the square root of scan rate (mV s⁻¹)^{1/2}, to determine the capacitive and intercalation contributions to the total charge storage. (d) Contribution ratio of the diffusion-controlled intercalation and surface-limited capacitive reaction as a function of the scan rate for the insertion reaction. (e) Current dependence on the square root of the square root of the square root of the scan rate for the diffusion coefficient.



Figure S10. The XRD patterns of the pristine electrode (black) and the charged electrode (blue) to 0.9 V vs. AC after 50 cycles.



Figure S11. Powder X-ray Le Bail fitting for the electrochemically Ca-inserted CMO sample of x = 0.50, recorded at room temperature.



Figure S12. Powder X-ray Le Bail fitting for the charged CMO sample of x = 0.07, recorded at room temperature.

	Mass ratio (%)			Relative atomic ratio		
-	Ca	Na	Mo	Ca	Na	Mo
Sample						
Na _{0.25} MoO ₃ ·(H ₂ O) _{0.49}	0.00	5.74	94.5	0.00	0.25	1.00
Ca _{0.13} MoO ₃ ·(H ₂ O) _{0.40}	5.15	0.00	94.9	0.13	0.00	1.00

Table S1. Elemental ratios estimated from ICP (Inductively Coupled Plasma) analysis for $Na_{0.25}MoO_3 \cdot (H_2O)_{0.49}$ and cation exchanged $Ca_{0.13}MoO_3 \cdot (H_2O)_{0.41}$ samples.

Table S2. Elemental ratios estimated from ICP (Inductively Coupled Plasma) analysis for the pristine (CMO), discharged, and charged samples.

	Mass ratio (%)			Relative atomic ratio		
	Ca	Na	Mo	Ca	Na	Mo
Sample						
Pristine	5.15	0.00	94.9	0.13	0.00	1.00
Discharged	17.2	0.00	82.8	0.50	0.00	1.00

x	Ato	mic %	Atomic ratio	
(estimated from charge	Ca	Мо	Ca/Mo	
transferred)				
Pristine				
0.13				
Sample 1	13.9	86.1	0.161	
Sample 2	11.2	88.8	0.126	
Sample 3	9.88	90.1	0.110	
Average	11.7	88.3	0.132	
(discharged) 0.29				
Sample 1	20.6	79.4	0.260	
Sample 2	20.2	79.8	0.253	
Sample 3	21.7	78.3	0.277	
Average	20.8	79.2	0.263	
(discharged) 0.45				
Sample 1	27.8	72.2	0.386	
Sample 2	27.5	72.5	0.380	
Sample 3	29.4	70.6	0.416	
Average	28.2	71.8	0.394	
(discharged) 0.61				
Sample 1	34.9	65.1	0.537	
Sample 2	32.5	67.5	0.481	
Sample 3	32.7	67.3	0.485	
Average	33.4	66.6	0.501	
(charged) 0.43				
Sample 1	26.7	73.3	0.364	
Sample 2	26.1	74.0	0.352	
Sample 3	26.0	74.0	0.351	
Average	26.2	73.8	0.356	
(charged) 0.25				
Sample 1	18.6	81.4	0.238	
Sample 2	16.8	83.2	0.202	
Sample 3	18.3	81.7	0.224	
Average	17.9	82.1	0.217	
(charged) 0.06				
Sample 1	9.01	91.0	0.099	
Sample 2	7.53	92.5	0.081	
Sample 3	8.20	91.8	0.089	
Average	8.20	91.8	0.090	

Table S3 Quantitative HR FE-SEM EDX data from which the (Ca/Mo) atomic ratios were estimated by the discharge capacity for each electrode sample of Ca_xMoO_3 ·(H₂O)_y (x = 0.13, 0.29, 0.45, 0.61, 0.43, 0.25, and 0.06; $y = 0.36 \sim 0.41$) during discharge/charge cycle.