Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information of

"A High Voltage Aqueous Proton Battery using an Optimized Operation of a MoO_3 Positive Electrode"

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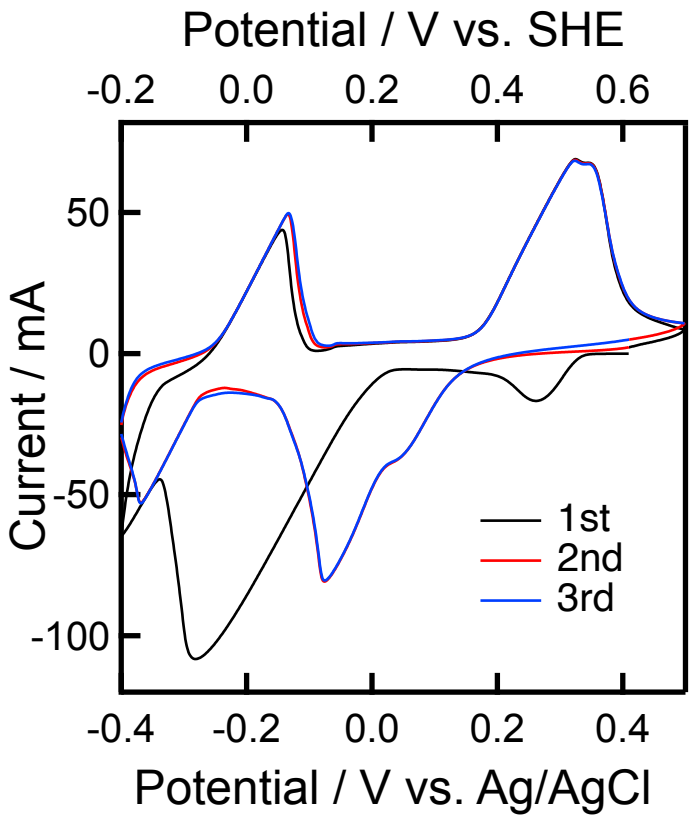


Figure S1. A cyclic voltammogram of the MoO_3 composite electrode at 10 mV sec^{-1} in 50 wt% H_2SO_4 aq.

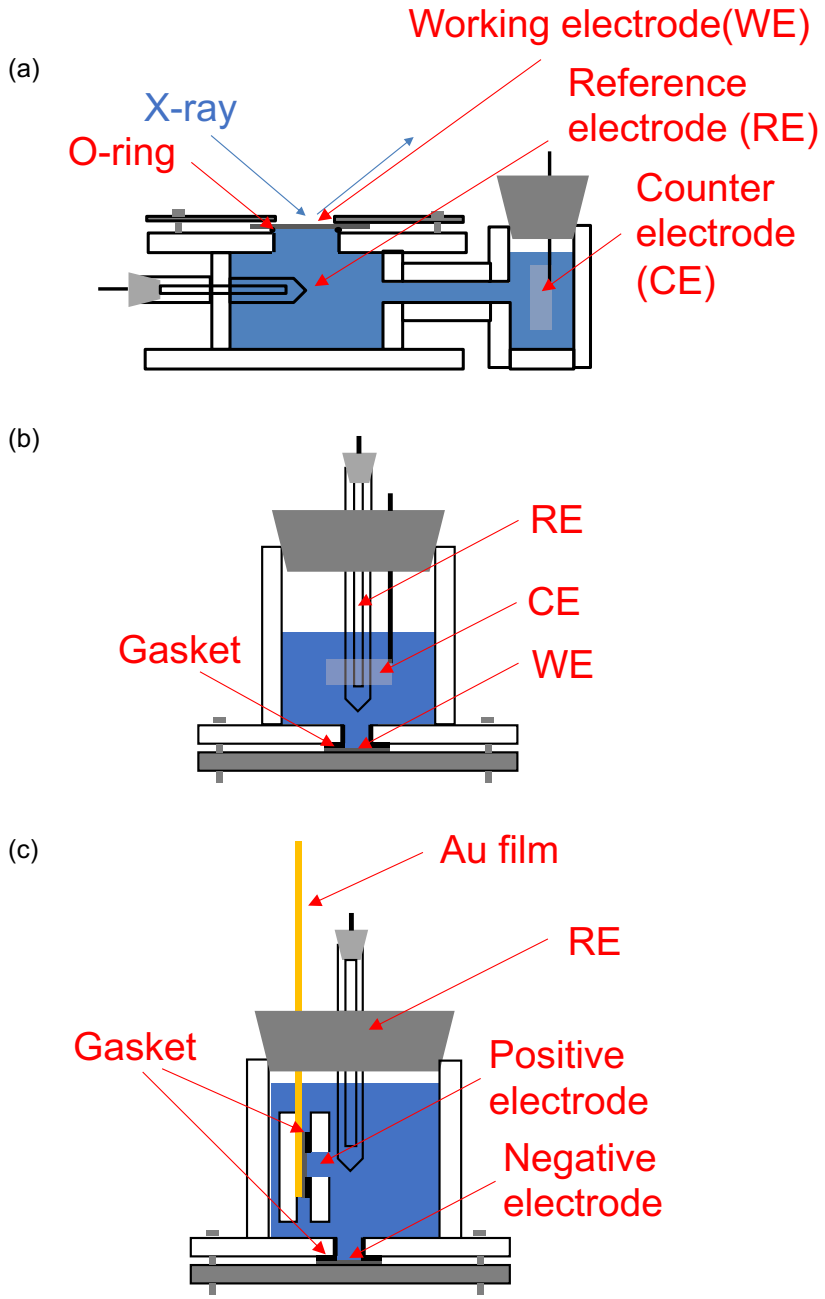


Figure S2. Schematics of electrochemical three-electrode half-cells for (a) operando X-ray diffraction and (b) charge-discharge measurements and (c) electrochemical three-electrode full-cells.

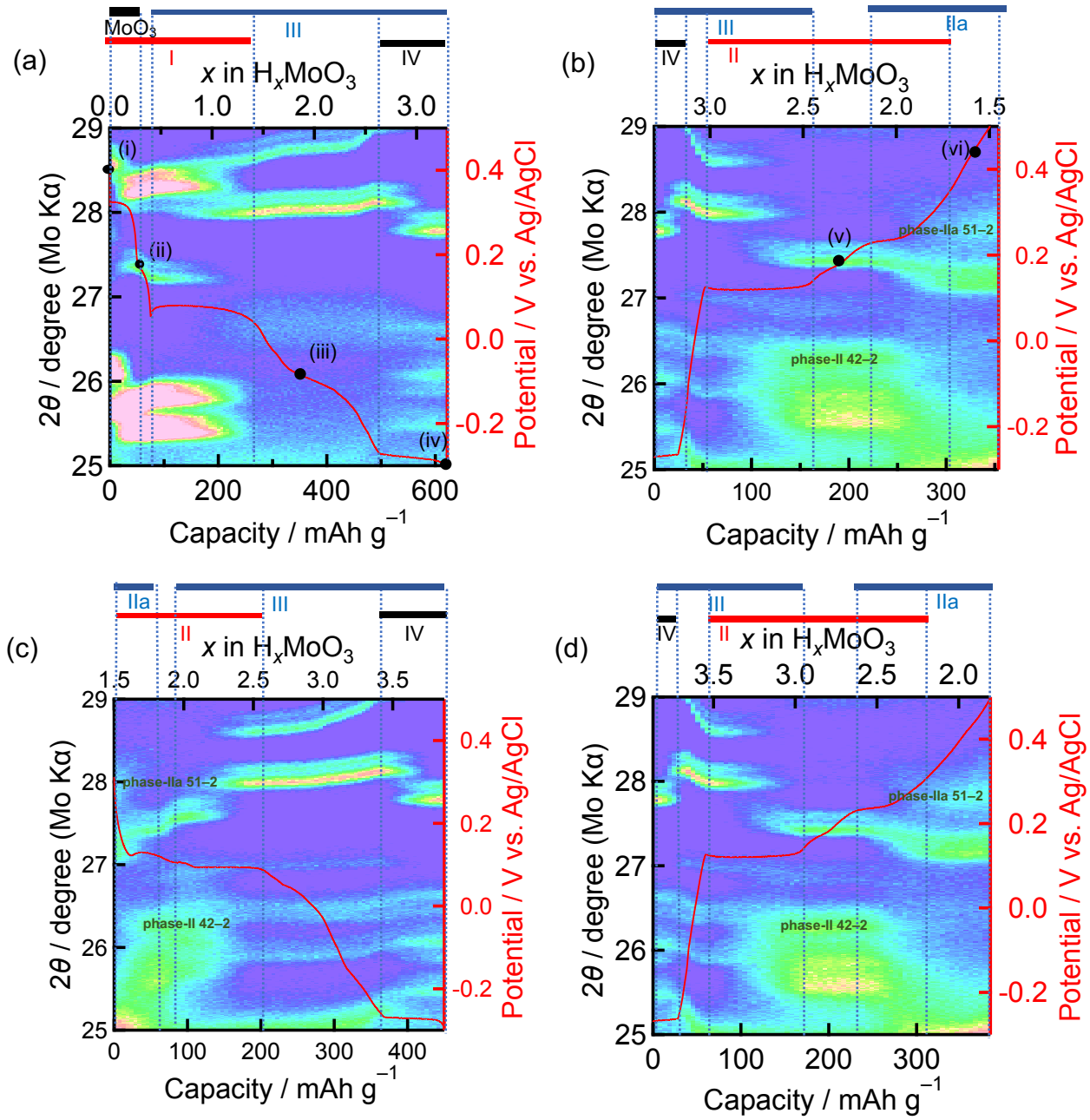


Figure S3. Operando XRD patterns of the MoO_3 electrode during reduction-oxidation in the potential range from –0.30 to 0.50 V at 100 mA g^{-1}; contour plots of (a) 1st reduction, (b) 1st oxidation, (c) 2nd reduction, and (d) 2nd oxidation.

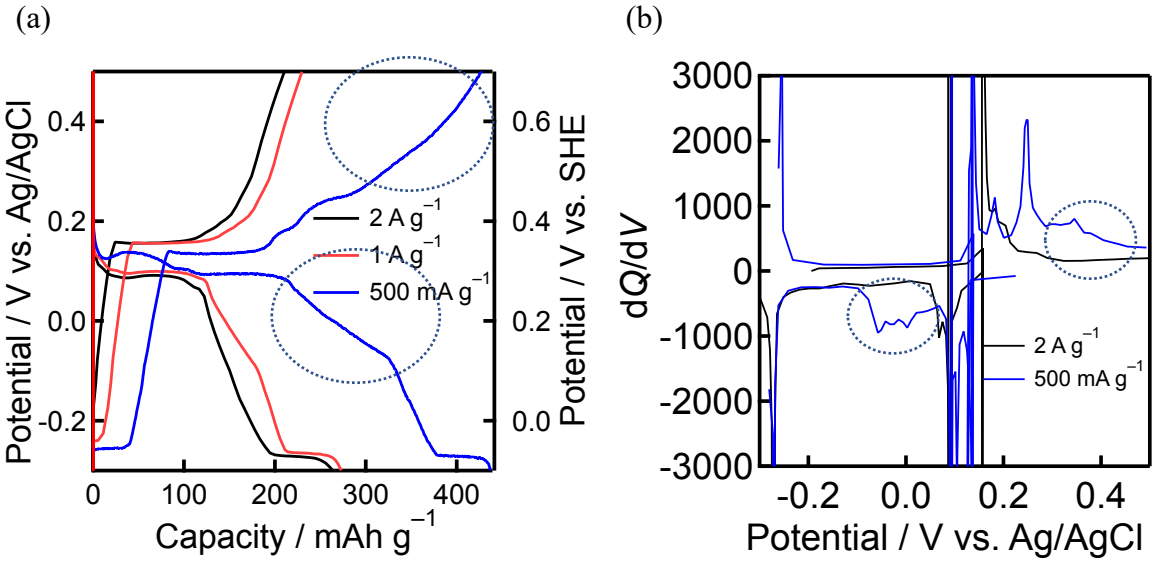
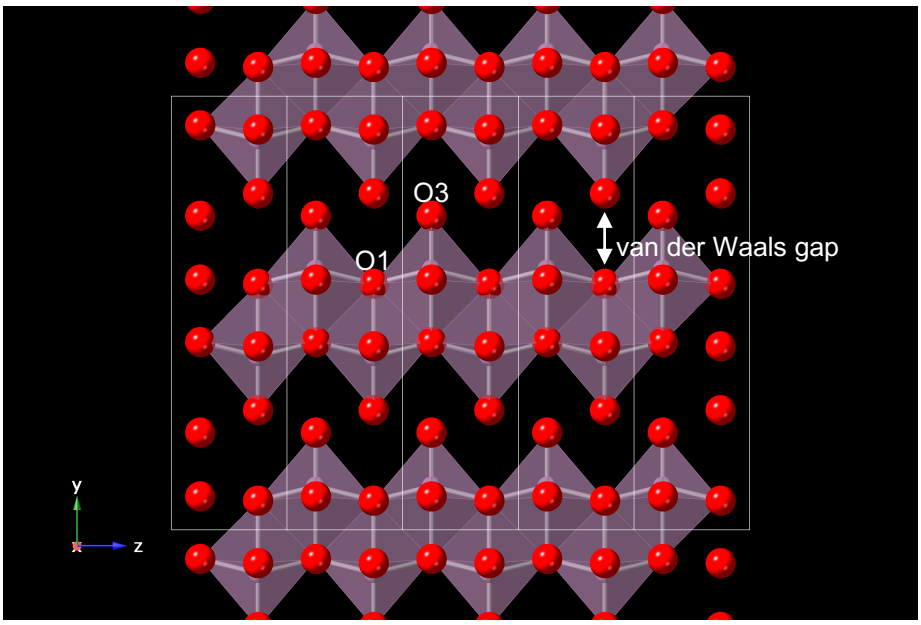


Figure S4. Charge-discharge property of the MoO_3 electrode in the potential range from –0.30 to 0.50 V; (a) charge-discharge curves; (b) dQ/dV plots. Dotted circles show the redox couple at around 0.3 and –0.1 V, which is only observed at low-rate reduction-oxidations (< 500 mA g^{-1}) as describe in the manuscript.

a) From a-axis



b) From c-axis

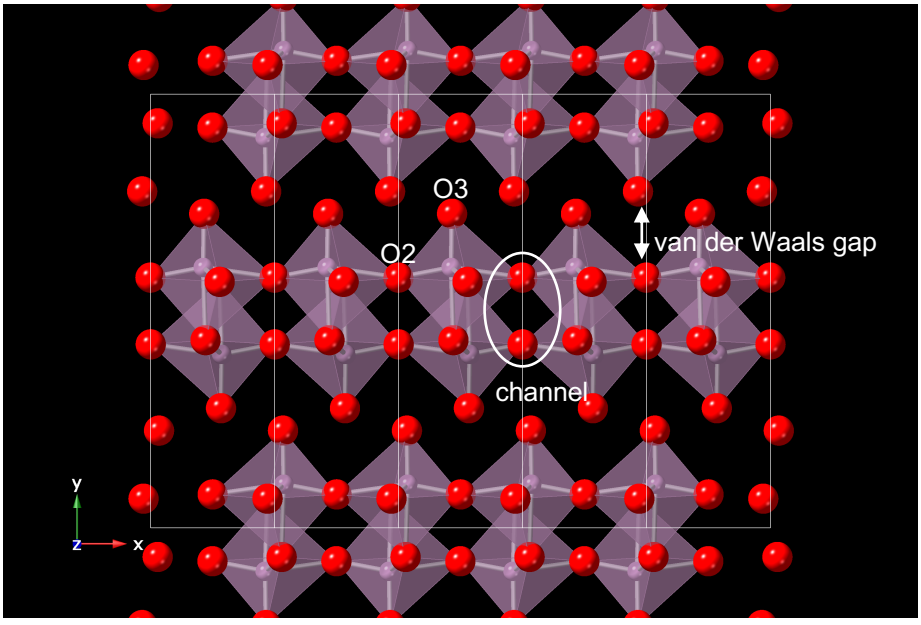


Figure S5. Schematic views of crystal structure of MoO_3. Purple polyhedral and red spheres denote MoO_6 octahedra and O atoms, respectively.

Table S1. Structure parameters of MoO_3.

	Calculated			Experimental [1]		
***a* / Å**		3.9105			3.9609	
(Error)		(-1.27%)				
***b* / Å**		15.5116			13.8570	
(Error)		(+11.94%)				
***c* / Å**		3.7304			3.6953	
(Error)		(+0.95%)				
Mo (4c)	0.0678	0.0957	1/4	0.075	0.1003	1/4
O1 (4c)	0.5016	0.4385	1/4	0.443	0.4328	1/4
O2 (4c)	0.5150	0.0820	1/4	0.501	0.0770	1/4
O3 (4c)	0.0308	0.2025	1/4	0.068	0.2242	1/4

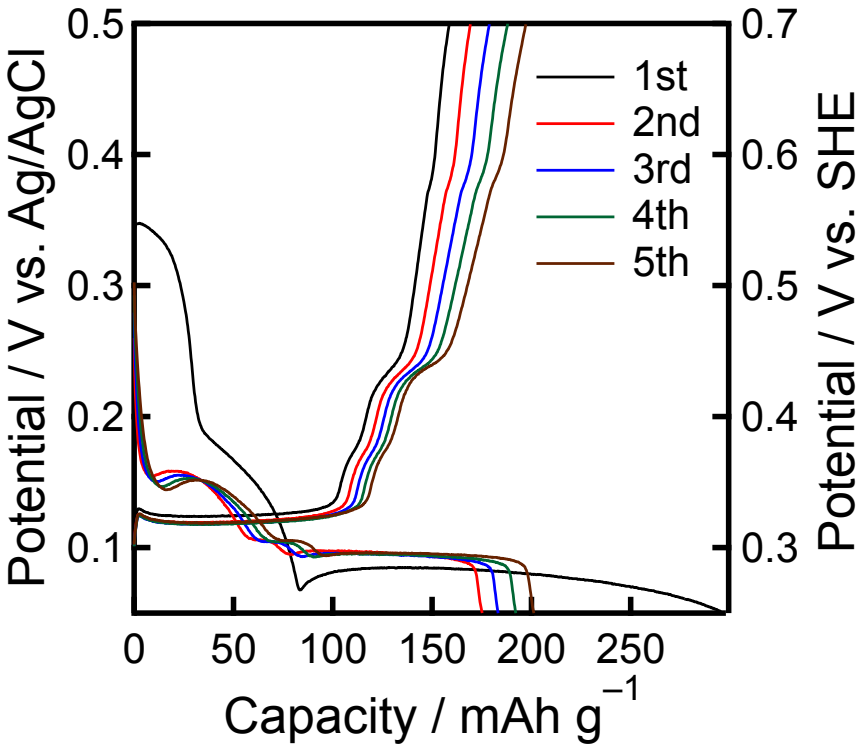


Figure S6. Charge-discharge curves of the MoO_3 electrode in the potential range from 0.05 to 0.50 V at 100 mA g^{-1}.

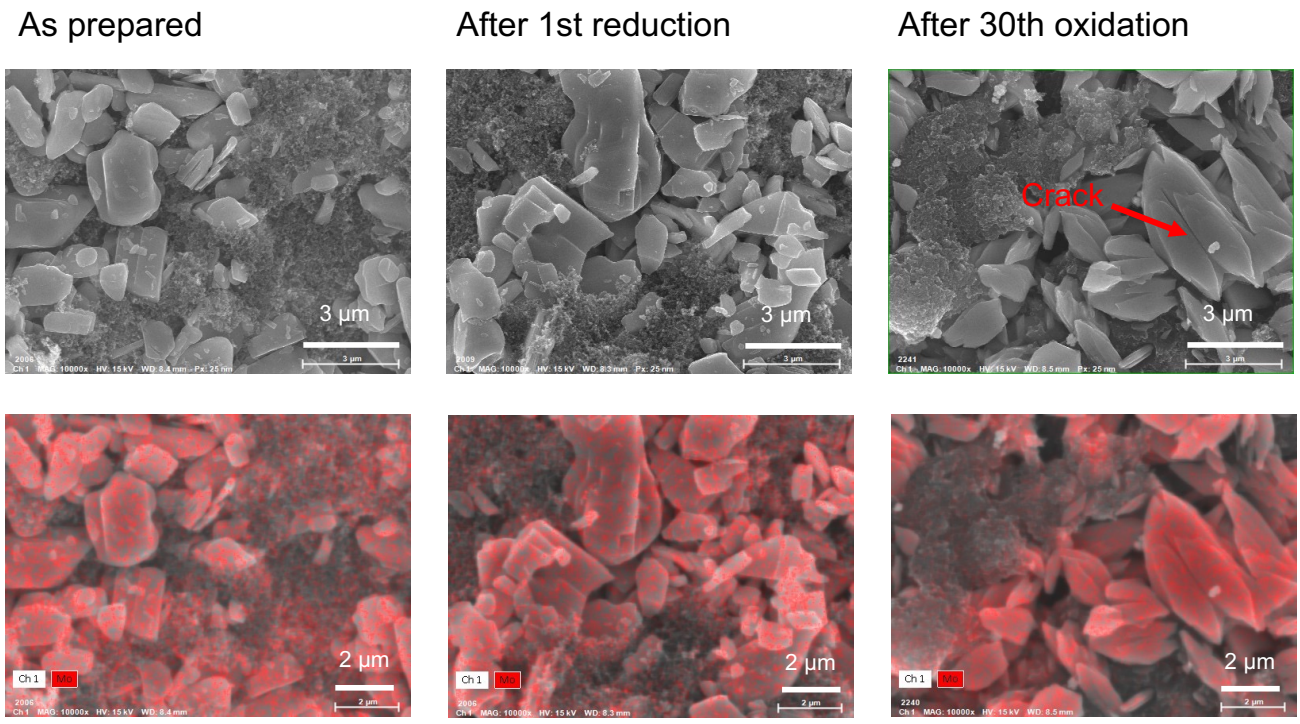


Figure S7. Ex-situ SEM images of the MoO_3 electrodes (upper). EDX maps of Mo element (red) (lower).

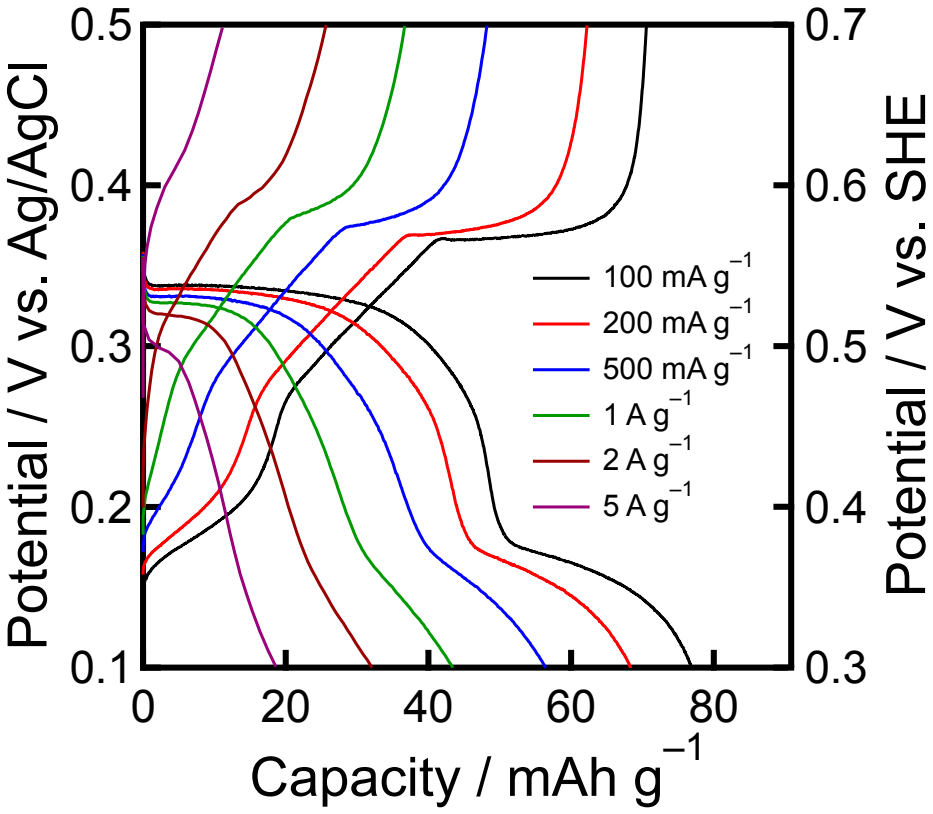


Figure S8. Reduction-oxidation curves of the MoO_3 electrode at different current densities.

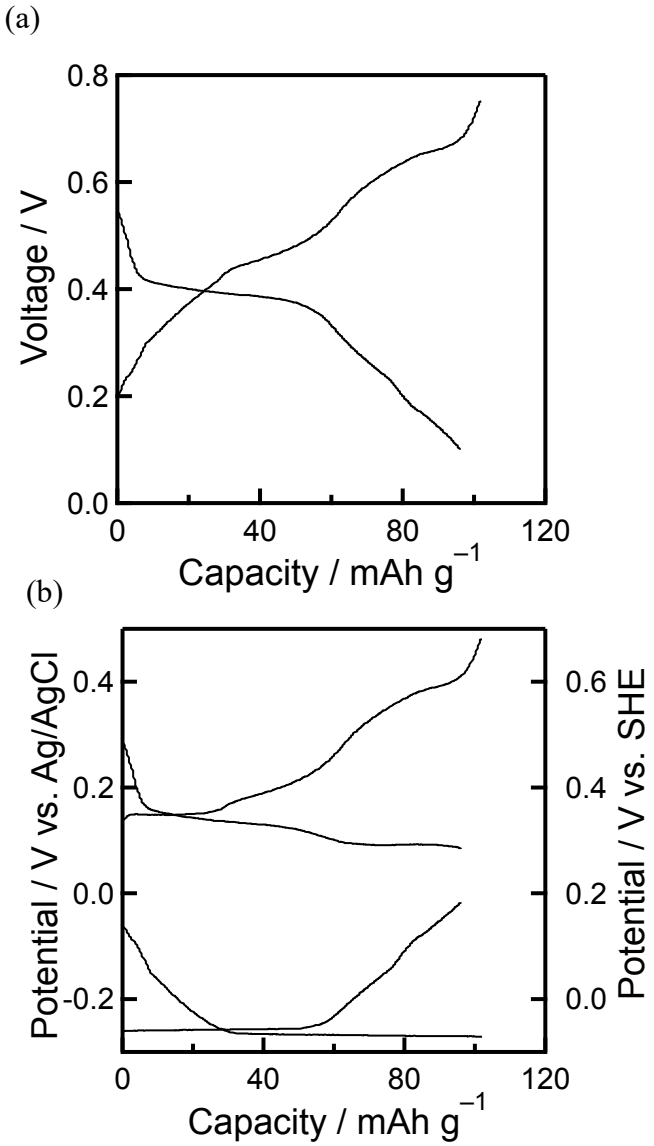


Figure S9. Charge-discharge property of the H_xMoO_3 (phase-IIa|phase-III)|50 wt% H_2SO_4|H_xMoO_3 (phase-III|Phase-IV) full-cell at 200 mA g^{-1}, 1st cycle; (a) cell voltage; (b) potentials of positive and negative electrodes. The capacities were calculated based on the mass of MoO_3 in one side of the electrode. The loading masses of the positive and negative electrodes were set to the same value. Before the full-cell construction, the positive and negative electrodes were electrochemically preconditioned with the half cells. The positive electrode was reduced and oxidized in the potential range from 0 to 0.5 V at 200 mA g^{-1} for 3 cycles, and the cycle was terminated at the reduced state. The negative electrode was reduced and oxidized in the potential range from –0.3 to 0.0 V at 100 mA g^{-1} for 3 cycles, and the cycle was terminated at the oxidized state. The average discharge voltage and energy density based on the total mass of the active materials are 0.33 V and 15 Wh kg^{-1}, respectively.

Table S2. Performances of the full cells shown in Fig. 5 and Fig. S9. The capacities during the first discharging and energy densities were calculated based on the total masses of the active materials.

Cell configuration	Capacity / mAh g^{-1}	Average voltage / V	Energy density / Wh kg^{-1}
MoO_3|phase-I|50 wt% H_2SO_4|phase-III|Phase-IV	36.5	0.48	17
phase-IIa|phase-III|50 wt% H_2SO_4|phase-III|Phase-IV	46.5	0.33	15

Reference

1. T. Leisegang, A.A. Levin, J.M. Walter, D.C. Meyer, Cryst. Res. Technol., 2005, **40**, 95-105.