Supporting information for

High-rate performance of H_xMoO₃ for aqueous aluminium-ion battery

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Experimental

A simple hydrothermal technique was used to prepare MoO₃ as outlined in reference [1 from ESI]. All the chemical reagents are analytical grade and they are used without further purification. In short, 0.6 g of ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄.4H₂O) was firstly dissolved in 36 ml of deionized water followed by continuous stirring. Then, a small amount (1 ml) of hydrochloric acid (HCl) was added slowly in the previous solution followed by stirring for 5 minutes. The final solution mixture was then transferred to a 50 ml Teflon lined autoclave and heated for 160 °C for 15 h. After that the solution was cooled naturally followed by washing with DI water and ethanol. The obtained precipitate was dried at 90 °C for 24 hour and the final product was procured. A similar kind of procedure was followed to obtain the hydrogen doped H_xMoO₃ wherein the volume of HCl was increased to 3.5 ml to facilitate enhanced doping keeping the other parameters same. For the full cell, commercially available LiMn₂O₄ is utilized.

The phase identification and the purity assessment of the as prepared samples were performed using X- ray diffraction and Raman spectroscopy. The morphology of the two samples was comprehensively analyzed using FESEM and HRTEM. X-ray photoelectron spectroscopy is performed to understand the formation of hydrogen doped H_xMoO_3 . High Score Plus 3.0d (3.0.4) software is used to index the crystallographic details.

The fabrication of the working electrode for electrochemical and morphological analysis was performed by preparing electrode slurries of active materials (MoO₃ and H_xMoO_3), carbon black and polyvinylidene fluoride in a weight ratio of 7:2:1 using N-methyl-2-pyrrolidone as solvent. The obtained slurry was cast on a piece of graphite and it was dried for 12 hours at 90° C.

The electrochemical activities of the MoO_3 and H_xMoO_3 were evaluated using cyclic voltammetry and galvanostatic charge discharge experiments in a three-electrode glass cell set up where Pt electrode and the Ag/AgCl electrode was used as counter and reference electrode respectively. The cyclic voltammetry analysis was conducted within a potential

window of -0.6 V to 0.5 V (vs Ag/AgCl) at different scan rates. Similarly, the chargedischarge profiles for both the materials were obtained within the same voltage range as CV measurements in current densities ranging from 2 Ag⁻¹ to 20 Ag⁻¹. The electrolytes used here were of various concentration of AlCl₃ and Al₂(SO₄)₃. The EIS was performed for both the materials in the frequency range of 1 mHz to 200 kHz with a signal amplitude of 10 mV. Calculation of Diffusion coefficient

From EIS:

The Diffusion coefficient (D $_{Al}^{3+}$) can be estimated from the following Equation (ref 22, 23 of main text):

$$D_{AI}^{3+} = 0.5 \left(\frac{RT}{An^2 F^2 C \sigma_w}\right)^2$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (298.15 K), A is the surface area of the electrode (0.25 cm²), n is the number of electrons transferred, F is Faraday constant (96500 C mol⁻¹), C is the concentration of Al³⁺ ion in the solution (1 M), and σ_w is the Warburg coefficient, calculated by the following Equation (at low-frequency region).

$$Z' = R_S + R_{CT} + \sigma_w \omega^{-0.5}$$

where R_S depicts electrolyte resistance, R_{CT} is the charge transfer resistance, σ_w can be obtained from the slope of linear fitting of the real part of impedance (Z') vs. the reciprocal square root of angular frequency ($\omega^{-0.5}$). The linear fitting is shown in figure S18 in the ESI below. The calculated diffusion coefficient for MoO₃ and H_xMoO₃ are 1.25 x 10⁻²¹ cm²S⁻¹ and 7.9 x 10⁻²¹ cm²S⁻¹ respectively (Figure S18).

From GITT:

The diffusion coefficient is estimated using the formula (ref 24 of main text):

$$D_{AI}^{3+} = \frac{4}{\tau\pi} (\frac{iV_m}{zFS})^2 (\frac{\Delta E_s}{\Delta E_t})^2$$

where i is the current (A), V_m is the molar volume of the electrode (cm³/mol), z is the charge number, F is the Faraday's constant (96485 C/mol), and S is the electrode area (cm²). ΔE_s corresponds to steady state voltage change and ΔE_s corresponds to voltage change during constant current pulse by single titration curve during discharge eliminating the iR drop. Here, the electrodes were discharged at a small constant current density of 0.1 mAcm⁻² followed by an open circuit relaxation of 1 minute to allow the cell in order to reach its steady state value (Figure 3e and S19). The operating voltage window was similar to the previous electrochemical measurements i.e from -0.6 V to 0.5 V.

Calculation of band gap from UV-visible data:

The Tauc's equation used here is (ref 7, 8 from ESI)

 $(\alpha h\nu)^{1/n} = A (h\nu - E_g)$

where, α is the absorption co-efficient, h is the plank's constant, v is the frequency, A is a constant, Eg is the energy and n is the number that characterize the transition process (n=1/2 for direct and 2 for indirect transitions). Figure S3 shows the calculated band gap for MoO₃ and H_xMoO₃ from the plot of $(\alpha hv)^{1/2}$ vs hv via extrapolation of the straight line to $(\alpha hv)^{1/2} = 0$ considering indirect allowed transitions [ref 18 from main text]. The obtained band gap values for MoO₃ and H_xMoO₃ are 3.89 eV and 3.6 eV respectively.

Calculation of energy density:

The calculation of energy density of the $LiMn_2O_4$ // H_xMoO_3 cell is based on following equations (ref 9 of ESI):

$$E = C \times V \times 1000 / m$$

Where E= energy density in Whkg⁻¹, C = Discharge capacity in mAh, V= average discharge voltage and m= total mass of cathode and anode (g). The estimated energy density of the cell is 18 Whkg⁻¹.

Supplementary figures



Figure S1. XRD patterns of (a) MoO_3 and H_xMoO_3 with crystallographic indexing, (b,c) enlarged view of the XRD patterns in the range of 11° -14° and 48° -51°.

S1.	Peak Position	Designation of the band	References
No.	(cm ⁻¹)		(in ESI)
	20.7 1		-
1	995 cm ⁻¹	corresponds to the terminal oxygen	2
	336 cm ⁻¹	(Mo ⁶⁺ =O) stretching mode	
2	897 cm ⁻¹	symmetric stretches of the terminal oxygen	3
3	818 cm ⁻¹	the doubly coordinated Mo ₂ =O bridging oxygen stretching modes	4
4	663 cm ⁻¹ and 465 cm ⁻¹	the triply coordinated Mo ₃ -O oxygen stretching mode	4
5	$200 - 600 \text{ cm}^{-1}$	MoO ₃ octahedral bending vibrations and lattice modes	5
6	236 cm ⁻¹ and 280 cm ⁻¹	the bending mode of Mo ₂ -O and the double bond (Mo=O) vibrations	5
7	373 cm ⁻¹	assigned to bending mode of Mo ₃ -O and Mo=O bending modes	5, 6

Table S1. Details of the characteristic Raman peaks observed in MoO₃.



Figure S2. a) FTIR spectra, XPS spectra of b) Mo3d, c) O1s; d) Full XPS spectra of MoO_3 and H_xMoO_3 .



Figure S3. UV visible spectra of a) MoO₃, b) H_xMoO₃, c) Tauc plot obtained from the UV visible data, d) PL spectra of MoO₃ and H_xMoO₃.



Figure S4. CV profile of MoO₃ in 1 M AlCl₃ aqueous electrolyte at a scan rate of 2.5 mVs⁻¹.

Phases	Electrolyte	Peaks	Peak	Peak
			positions	Separatio
			(V)	ns (V)
MoO ₃	1 M AlCl ₃	А	0.15	0.24
		A'	-0.09	
		В	-0.31	0.27
		B'	-0.4	
		С	-0.5	0.53
		C'	-0.58	
H _x MoO ₃	1 M AlCl ₃	Х	-0.01	0.19
		X'	-0.2	
		Y	-0.45	0.07
		Y'	-0.52	
MoO ₃	0.5 M	E	0.19	0.35
	$Al_2(SO_4)_3$	E'	-0.16	
		F	-0.25	0.22
		F'	-0.47	
H _x MoO ₃	0.5 M	G	0.13	0.31
	$Al_2(SO_4)_3$	G'	-0.18	
		Н	-0.31	0.17
		H'	-0.48	

Table S2: Peak to peak separation from Cyclic Voltammetry



Figure S5. CV profile of a) MoO₃ and b) H_xMoO_3 , c) Superimposition of the CV scan of MoO₃ and H_xMoO_3 in Al₂(SO₄)₃ aqueous electrolyte at a scan rate of 2.5 mVs⁻¹.



Figure S6. Galvanostatic charge-discharge measurements of MoO₃ at current density of a) 5 Ag⁻¹, b) 10 Ag⁻¹, c) 20 Ag⁻¹ in 1 M aqueous AlCl₃ electrolyte.



Figure S7. Rate performance of MoO_3 at current density of a) 5 Ag⁻¹ and b) 10 Ag⁻¹ in 1 M aqueous AlCl₃ electrolyte.



Figure S8. Galvanostatic charge-discharge measurements of H_xMoO_3 at current density of a) 5 Ag⁻¹, b) 10 Ag⁻¹, c) 20 Ag⁻¹ in 1 M aqueous AlCl₃ electrolyte.

Electrolyte	Current	Phases	1 st D	1 st C	50 th D	50 th C
	density		(mAhg-1)	(mAhg-	(mAhg-1)	(V)
				1)		(mAhg-
						1)
1 M AlCl ₃	2 Ag-1	MoO ₃	274	137	105	76
		H _x MoO ₃	417	196	132	120
	5 Ag-1	MoO ₃	221	115	80	73
		H _x MoO ₃	260	148	120	100
	10 Ag-1	MoO ₃	180	103	80	70
		H _x MoO ₃	247	140	119	100
	15 Ag-1	MoO ₃	174	90	80	74
		H _x MoO ₃	224	120	112	102
	20 Ag-1	MoO ₃	97	50	50	46
		H _x MoO ₃	193	119	107	102

Table S3- Specific Capacities after discharge and charge



Figure S9. Comparison of 2^{nd} cycle of galvanostatic charge-discharge measurements of MoO₃ and H_xMoO₃ at current density of a) 2 Ag⁻¹, b) 5 Ag⁻¹, c) 10 Ag⁻¹ and d) 20 Ag⁻¹ in 1 M aqueous AlCl₃ electrolyte.

Electrolyte	Current density	Phases	Discharge(V)	Charge (V)	Peak Separations (V)
1 M AlCl ₃	2 Ag-1	MoO ₃	-0.09	0.18	0.27
		H _x MoO ₃	-0.13	-0.02	0.11
	5 Ag-1	MoO ₃	-0.08	0.15	0.23
		H _x MoO ₃	-0.06	0.09	0.15
	10 Ag-1	MoO ₃	-0.16	0.11	0.27
		H _x MoO ₃	-0.05	0.14	0.19
	15 Ag-1	MoO ₃	-0.19	0.19	0.38
		H _x MoO ₃	-0.17	0.17	0.34
	20 Ag-1	MoO ₃	-0.4	0.16	0.56
		H _x MoO ₃	-0.25	0.18	0.43

Table S4: Plateau separation from GCD



Figure S10. CV profiles of H_xMoO₃ in 1 M H₂SO₄ aqueous electrolyte at different scan rates.



Figure S11. FESEM images of H_xMoO₃: a) 1st Discharge and b) 1st Charge



Figure S12. Galvanostatic charge-discharge measurements of MoO₃ at current density of a) 2 Ag⁻¹, b) 5 Ag⁻¹ and c) 10 Ag⁻¹ in 0.5 M aqueous Al₂(SO₄)₃ electrolyte.



Figure S13. Galvanostatic charge-discharge measurements of H_xMoO_3 at current density of a) 2 Ag⁻¹, b) 5 Ag⁻¹ and c) 10 Ag⁻¹ in 0.5 M aqueous Al₂(SO₄)₃ electrolyte.



Figure S14. Rate performance of MoO₃ at current density of a) 2 Ag⁻¹, b) 5 Ag⁻¹ and c) 10 Ag⁻¹ in 0.5 M aqueous Al₂(SO₄)₃ electrolyte.



Figure S15. Rate performance of H_xMoO_3 at current density of a) 2 Ag⁻¹, b) 5 Ag⁻¹ and c) 10 Ag⁻¹ in 0.5 M aqueous Al₂(SO₄)₃ electrolyte.



Figure S16. a) CV profile of the $LiMn_2O_4$ // H_xMoO_3 cell at a scan rate of 2.5 mVs⁻¹. Galvanostatic charge-discharge measurements at current density of b) 80 mAg⁻¹ and c) 250 mAg⁻¹, Rate performance at d) 80 mAg⁻¹, e) 250 mAg⁻¹ of the cell.

SI/	Phases	Discharge	R ₁	R ₂	R ₃
No		State	(Ohm.cm ⁻	(Ohm.cm ⁻	(Ohm.cm ⁻
		State	²)	²)	²)
1	MoO ₃	1D	Const	29435	4976
		100D	Const	10 683	1913
2	H _x MoO ₃	1D	Const	14 170	2 968
		100D	Const	9 719	186.3

Table S5: Charge transfer resistance (R_3) values from EIS fitting

 \mathbf{R}_{1} : Solution / Ohmic resistance (\mathbf{R}_{sol})

 R_2 : Electrode Interface's resistance ($R_{Interface}$)

R₃: Charge transfer resistance (R_{ct})



Figure S17. The relationship between Z' and $\omega^{-1/2}$ in the low-frequency region.



Figure S18. a) Demonstration of a single titration step during discharged state of H_xMoO_3 , b) enlarged view of one portion of the discharge curve with measured titration step highlighted on it; c) GITT measurement of MoO_3 for one complete cycle, d) demonstration of a single titration step during discharged state of MoO_3



Figure S19. (a) XRD patterns of H_xMoO_3 after cycling, enlarged view of the XRD patterns in the range of (b) $10^{\circ} - 35^{\circ}$ and (b) $33^{\circ} - 35^{\circ}$ of discharged state electrode



Figure S20. a,b) HRTEM images and fringe patterns (inset) of discharged state electrode of H_xMoO_3

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