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MgAl Layered Double Hydroxide as a New Transition Metal Free Anode for Lithium-ion Batteries

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Experimental details

Materials

The analytically pure $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, N-methyl-1,2-pyrrolidone (NMP) and urea were purchased from Aladdin Co. Ltd. and used without any additional processing. The lithium foils and electrolyte consisted of 1 M LiPF_6 in a 1:1:1 mixture of ethylene carbonate (EC), methyl ethyl carbonate (EMC) and dimethyl carbonate (DMC) with 1% VC were obtained from DodoChem Co. Ltd. Shenzhen Kejing Co. Ltd. offered Carbon ECP600JD (marked as ECP) as a conductive agent and polyvinylidene fluoride (PVDF) as the binder.

Synthesis of $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH

The $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH was prepared by a simple hydrothermal method. 0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.1M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.0 M urea were dissolved in 800 ml deionized water and stirred for 5 min. And then, the above solution was transferred into 80 ml Teflon autoclaves and reacted at 110 °C for 24 hours. After cooling down to room temperature, the obtained product was washed with deionized water and ethanol several times at 3000 rpm for 8 min. Subsequently, the powder $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH was gained by drying in an oven at 60 °C overnight.

Assembly of the Li half cell

$\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH, ECP, and PVDF were mixed with the mass ratio of 7:2:1 in vibration ball mill for 4 minutes and NMP was used as a solvent to adjust the viscosity of the slurry. Then the slurry was coated on Cu foil with 100 μm blade and dried at 90 °C overnight under vacuum to evaporate NMP. The dried Cu foil was

sliced into pieces with diameter of 12 mm. The Li half cell was assembled into a 2032 coin-type battery with a reasonable amount of LiPF₆ electrolyte in an argon-filled glove box with water/oxygen content lower than 0.1 ppm.

Sample Characterizations

X-ray diffraction (XRD) patterns of LDH powder and cycled electrodes were tested by Rigaku XRD-6000 diffractometer at 40 kV and 30 mA with Cu K α radiation ($\lambda = 0.15418$ nm), accepting a scanning rate of 10° min⁻¹ for LDH powder and 2° min⁻¹ for cycled electrodes. At an accelerating voltage of 10 kV, Zeiss Supra 55 field emission scanning electron microscope (SEM) was used to obtain the morphology of Mg₂Al₁-CO₃ LDH powder sample and cycled electrodes. Fourier transform infrared (FTIR) spectra were acquired by using a Vector 22 (Bruker) spectrophotometer under 2 cm⁻¹ resolution. Inductively coupled plasma (ICP) emission spectroscopy was measured on Shimadzu ICPS-7500 to ensure the element ratio in Mg₂Al₁-CO₃ LDH. Using Al K α as exciting illuminant, X-ray photoelectron spectrometer (XPS) was acquired on Escalab 250 to observe the valence of elements. In Ar atmosphere, thermogravimetry and derivative thermogravimetry (TG-DTG) analysis was conducted on PCT-1A thermal analysis system with a heating rate of 10 °C/min. A CHI660C type electrochemical workstation and LAND battery test system were applied for electrochemical performance test and kinetic characterization. The diffusion coefficient of Li⁺ (D_s) was calculated by galvanostatic intermittent titration technique (GITT) based on the following equation:

$$D_s = \frac{4}{\pi} \frac{mV}{\tau(MA)^2} \frac{\Delta E_s}{(\Delta E_t)^2} \quad (1)$$

where m (g) and M (g mol^{-1}) are the mass and molecular weight of $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH; τ (s) is constant current pulse time; V ($\text{cm}^3 \text{mol}^{-1}$) is assigned to the molar volume; A (cm^2) is the surface area of the electrode; ΔE_s (V) and ΔE_t (V) represent the voltage change between the two relaxations and voltage change caused by the pulse. Pulse current density is 50 mA g^{-1} with $\tau = 10 \text{ min}$, and a relaxation time of 1 h.

Supplementary figures

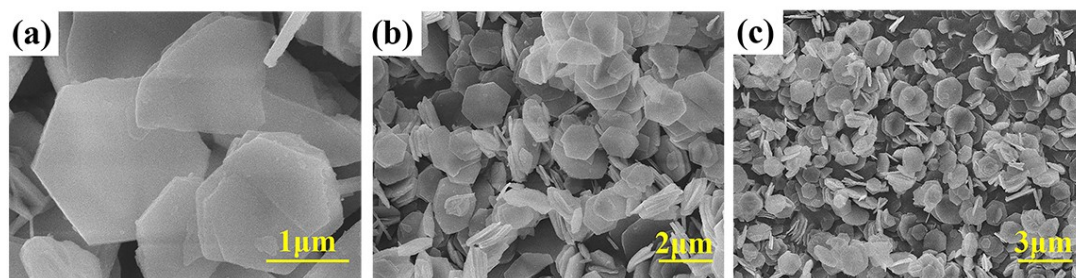


Fig. S1 SEM images of Mg₂Al₁-CO₃ LDH in different magnifications.

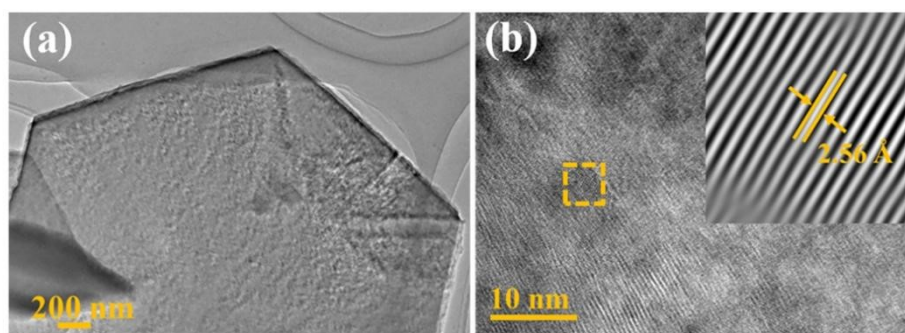


Fig.S2 (a) TEM image of Mg₂Al₁-CO₃ LDH; (b) High-resolution TEM image for Mg₂Al₁-CO₃ LDH (inset: Enlarged high-resolution TEM image from selected area).

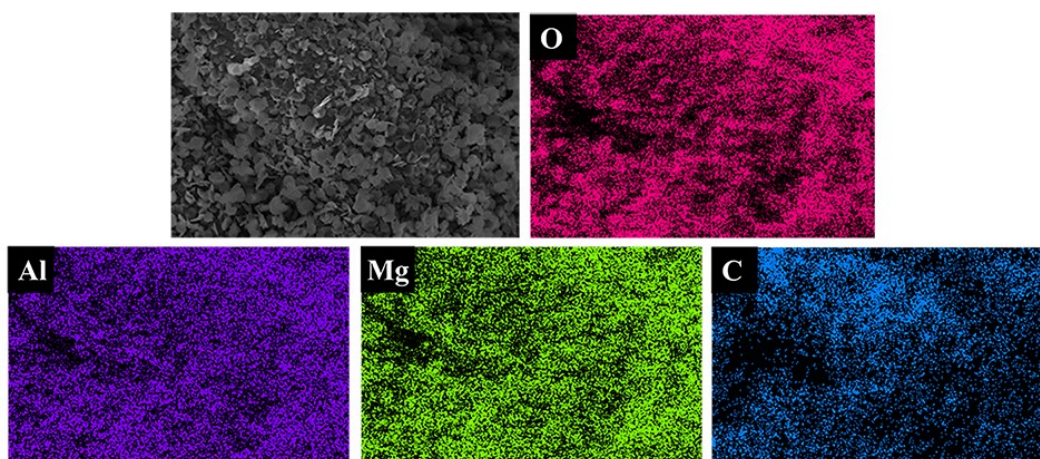


Fig. S3 EDS mappings of Mg₂Al₁-CO₃ LDH.

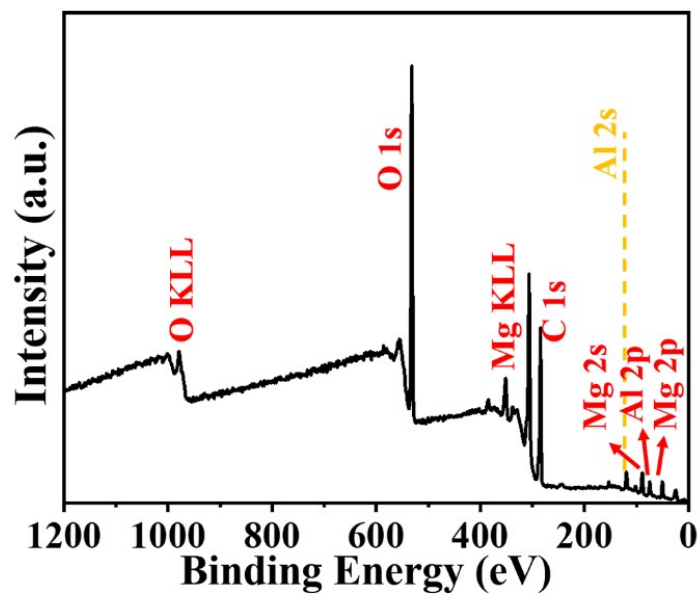


Fig. S4 XPS survey of the $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH.

Table. S1 FTIR peaks attribution of $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH in Fig. 1c.

Wavenumber (cm^{-1})	Attribution
3431	O–H stretching mode
3032	$\text{H}_2\text{O-CO}_3^{2-}$ bridge vibration
1579	HOH bending mode
1400/1356	CO_3^{2-} antisymmetric stretching mode
870	CO_3^{2-} bending mode
784	O–H translational vibration
694	CO_3^{2-} antisymmetric bending mode
558	Mg–O translational vibration
447	Al–O bending mode

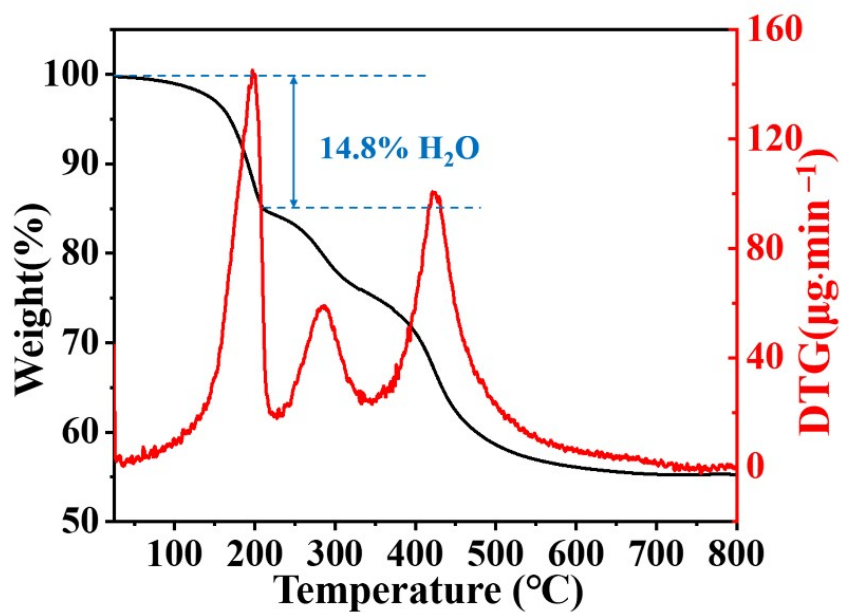


Fig. S5 TG-DTG curve of Mg₂Al₁-CO₃ LDH from room temperature to 800 °C.

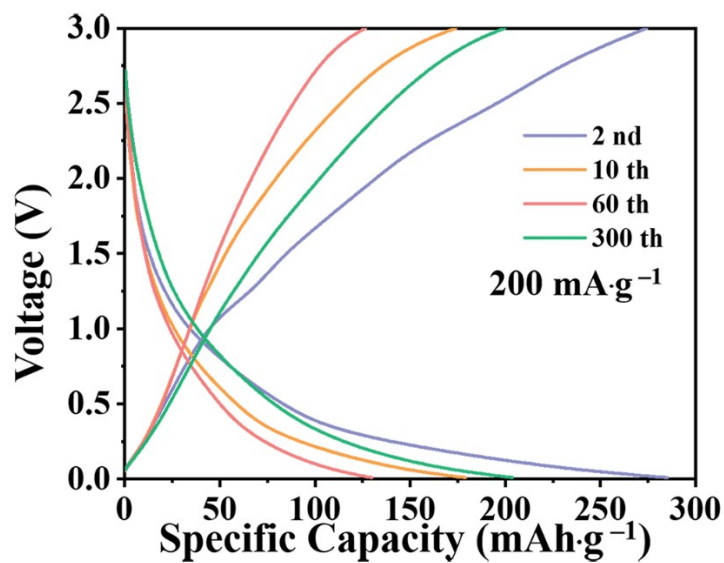


Fig. S6 The GCD curves of different cycles at 200 mA·g⁻¹.

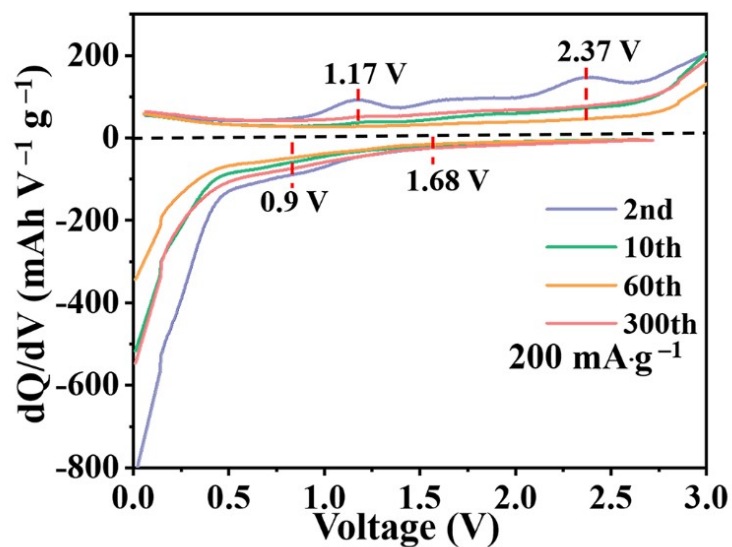


Fig. S7 dQ/dV curves of 2nd, 10th, 60th and 300th cycles.

Table. S2 The comparison of the rate performance between Mg₂Al₁-CO₃ LDH and other reported LDH electrodes in LIBs.

Materials	Specific capacity at different current density(mAh·g ⁻¹)			
	50 mA·g ⁻¹	100 mA·g ⁻¹	200 mA·g ⁻¹	1000 mA·g ⁻¹
NiAl LDH ^[1]	1324	827	668	/
CoNi LDH ^[2]	1743.6	/	/	33
NiFe LDH/rGO ^[3]	/	958.7	835	/
Ni ₂ Co LDH ^[4]	1028	755	532	90
This work	227	166.5	134.6	73

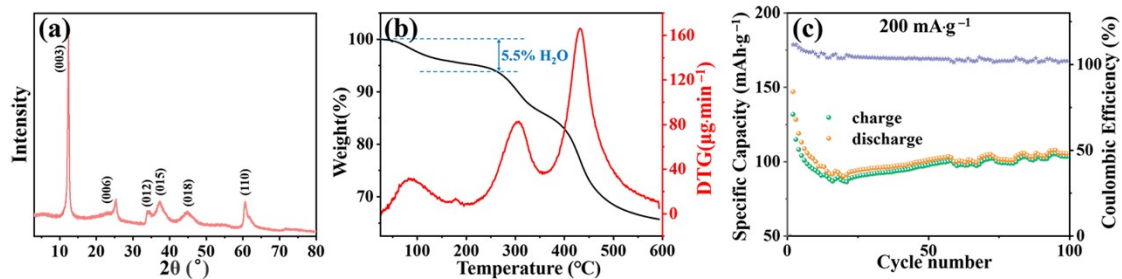


Fig. S8 (a) The XRD pattern of water-deficient $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH; (b) TG-DTG curves of water-deficient $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH from room temperature to 600 °C; (c) long cycling performance of water-deficient $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH.

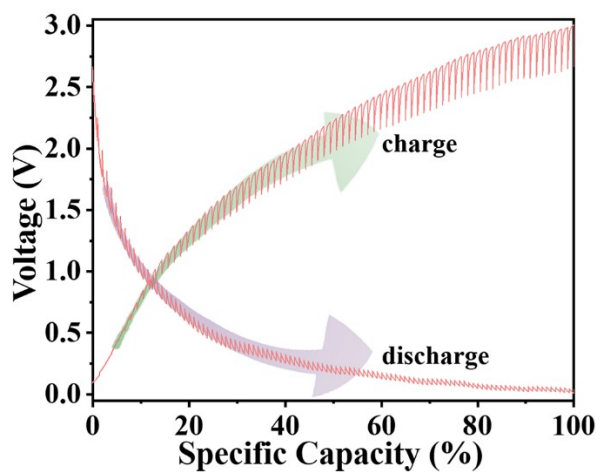


Fig. S9 Charge/discharge curves in the GITT test.

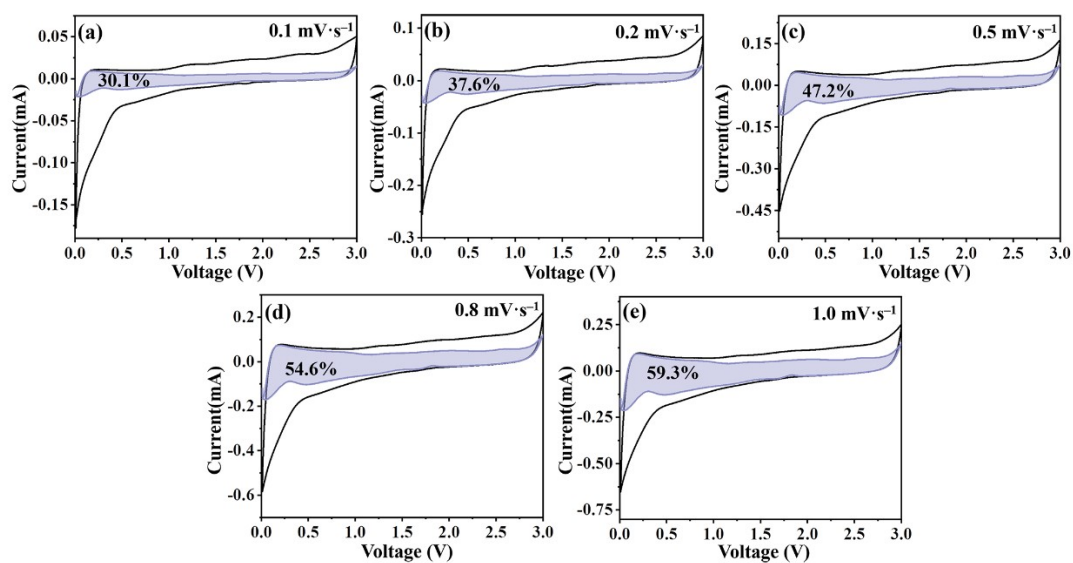


Fig. S10 (a)-(e) Pseudocapacitance ratios at scanning rates of 0.1, 0.2, 0.5, 0.8 and 1 $\text{mV}\cdot\text{s}^{-1}$, respectively.

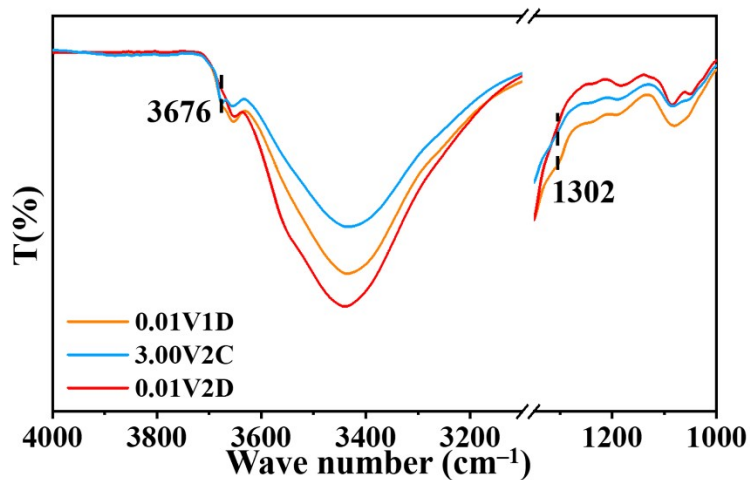


Fig. S11 FTIR spectra of cycled $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH electrode at 0.01V1D, 3.00V2C and 0.01V2D. 1D, 2C and 2D mean the discharge process of 1st circle, the charge process of 2nd circle and the discharge process of 2nd circle, respectively.

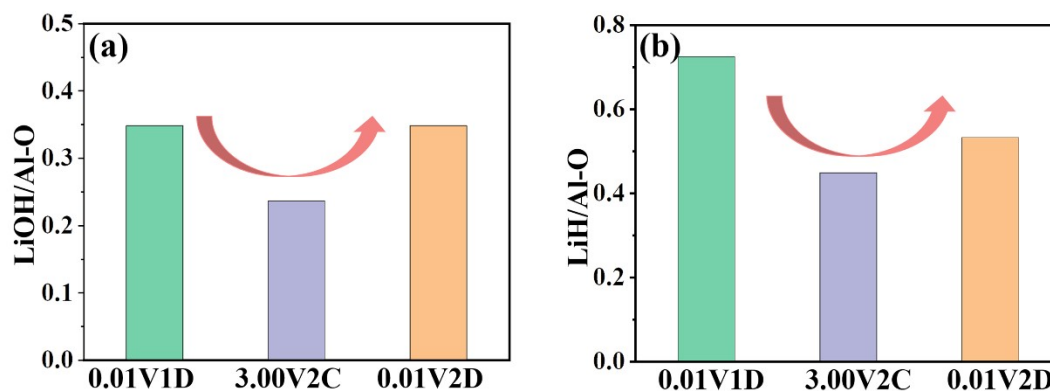


Fig. S12 (a) Intensity ratio of LiOH and Al–O at 0.01V1D, 3.00V2C and 0.01V2D. (b) Intensity ratio of LiH and Al–O at 0.01V1D, 3.00V2C and 0.01V2D. 1D, 2C and 2D mean the discharge process of 1st circle, the charge process of 2nd cycle and the discharge process of 2nd cycle, respectively.

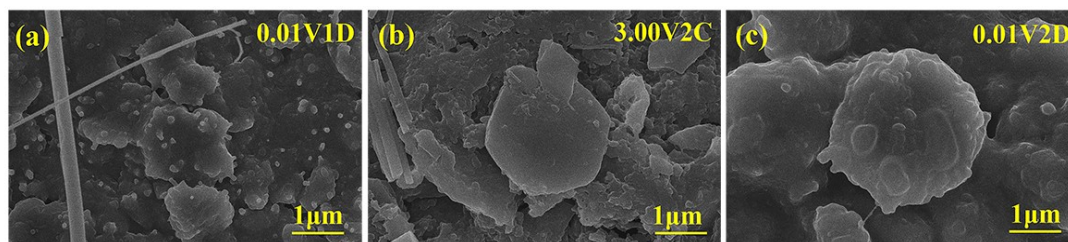


Fig. S13 (a)-(c) SEM images of cycled $\text{Mg}_2\text{Al}_1\text{-CO}_3$ LDH electrode at 0.01V1D, 3.00V2C and 0.01V2D. 1D, 2C and 2D mean the discharge process of 1st cycle, the charge process of 2nd circle and the discharge process of 2nd cycle, respectively.

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