Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Thermodynamics and kinetics of Mg^{2+}/Li^{+} and Mg^{2+}/Na^{+} co-intercalation into layered titanium disulfide

Yudi Tang[a], Donggang Tao[a], Yuliang Cao[b], Fei Xu*[a]

[a] Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China.

[b] Hubei Key Lab of Electrochemical Power Sources, College of Chemistry & Molecular Science, Wuhan University, Wuhan 430072, China.

* E-mail: Fei Xu (xufei2058@whu.edu.cn)

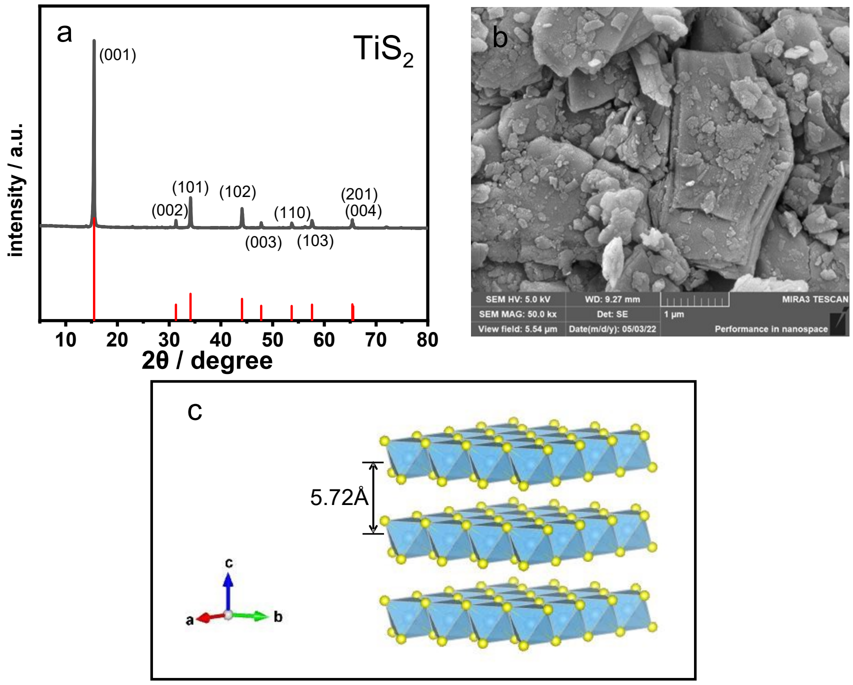

Fig. S1 (a) XRD pattern, (b) SEM image and (c) crystal structure of TiS_2. The TiS_2 layer consists of two layers of S atoms, in which Ti atoms occupy the octahedral positions. The TiS_2 layers form a 2D layered structure connected by van der Waals forces, and the *c* parameter is 5.72 Å (Fig. S1c). The characteristic XRD peak at 15.7° is ascribed to the (001) plane.

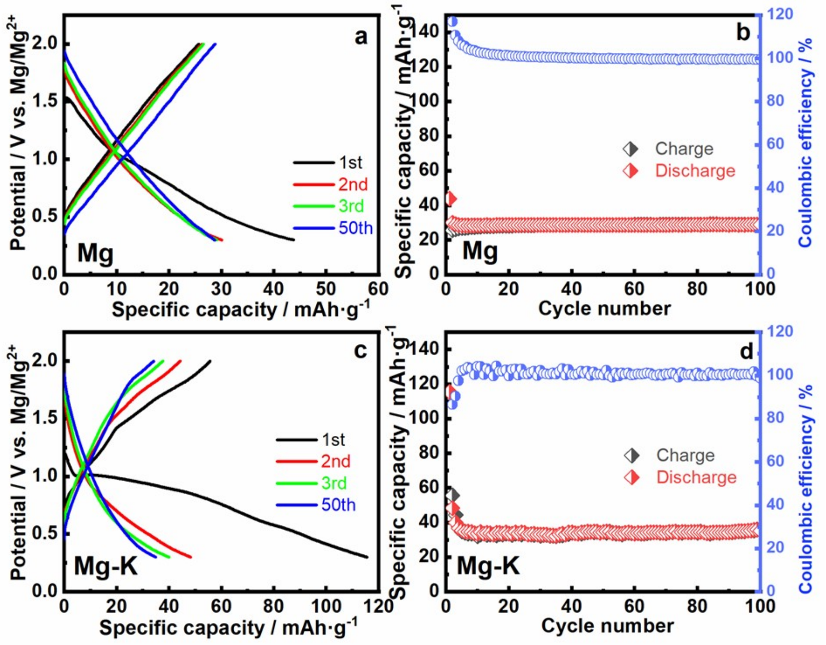

Fig. S2 (a) Charge/discharge profiles and (b) cycling performance at 50 mA g^{-1} of the Mg battery. (c) Charge/discharge profiles and (d) cycling performance at 50 mA g^{-1} of the Mg^{2+}/K^+ battery.

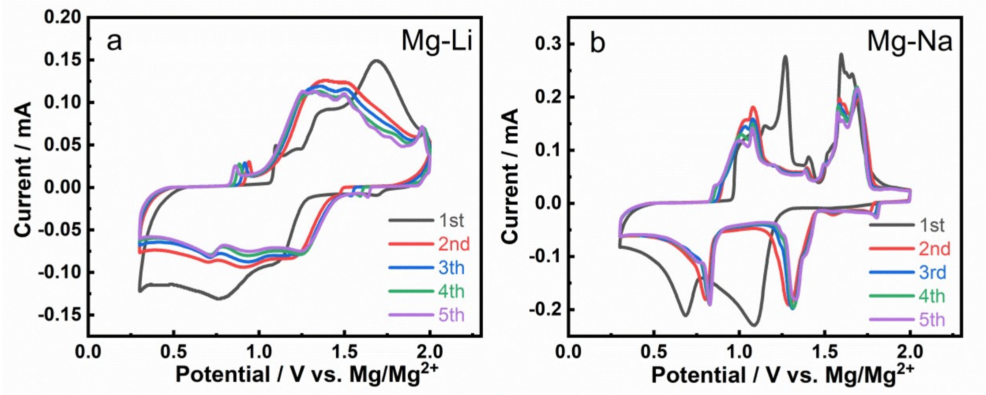

Fig. S3 CV profiles at 0.1 mV s^{-1} of TiS_2 in (a) Mg^{2+}/Li^+ and (b) Mg^{2+}/Na^+ electrolytes. The difference of the CV curves between the first cycle and the subsequent cycles might be owing to the formation of SEI on the TiS_2 cathode or Mg anode.

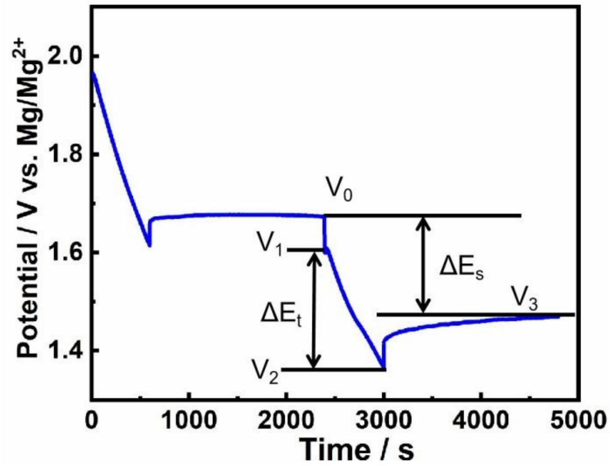

Fig. S4 GITT calculation details.

$$D = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)^2\left(\frac{\Delta E_S}{\Delta E_t}\right)^2$$

τ (=600 s) —— the duration of the current pulse;

n_m (mol) —— the number of moles;

V_m (=33.19 cm^3/mol)—— the molar volume of the electrode;

S (=1.131 cm^2) —— the electrode area;

ΔE_s (V) —— the steady-state voltage change,

ΔE_t (V)——the voltage change during the constant current pulse, eliminating the iR drop.

Table S1. Calculation details for formation energies (ΔE) of different intercalation structures.

Reference system	E(total)	multiple	E(everge)
TiS_2	–19.776	1.0000	–19.776
Na	–2.6109	2.0000	–1.3054
Mg	–2.9979	2.0000	–1.4990
Li	–3.8032	2.0000	–1.9016

	E(total)	Na	Mg	Li	TiS_2	ΔE(eV)
$NaMg_{0.5}(TiS_2)_2$-case1	–88.146	2.0000	1.0000	0.0000	4.0000	–1.6442
$NaMg_{0.5}(TiS_2)_2$-case2	–176.31	4.0000	2.0000	0.0000	8.0000	–1.6465
$LiMg_{0.5}(TiS_2)_2$-case1	–90.276	0.0000	1.0000	2.0000	4.0000	–1.9569
$LiMg_{0.5}(TiS_2)_2$-case2	–180.56	0.0000	2.0000	4.0000	8.0000	–1.9582
$LiTiS_2$	–23.598	0.0000	0.0000	1.0000	1.0000	–1.9210
$Na_3(TiS_2)_{10}$	–415.57	6.0000	0.0000	0.0000	20.0000	–2.0376
$Mg(TiS_2)_2$	–254.36	0.0000	6.0000	0.0000	12.0000	–1.3426

$$\Delta E = [E(total) - xE(TiS2) - yE(Li) - zE(Mg) - mE(Na)]/(y + z + m)$$

The reference frame locates TiS_2, Li-bulk Na-bulk Mg-bulk, and we can calculate the energy of E(TiS_2), E(Li), E(Mg) and E(Na). Therefore, by calculating the average formation energy of each structure, the difficulty of formation could be estimated. The more negative the formation energy value, the easier it is to form. The formation energy for different intercalation structures can be described as:

$$\Delta E = [E(total) - xE(TiS2) - yE(Li) - zE(Mg) - mE(Na)]/(y + z + m)$$

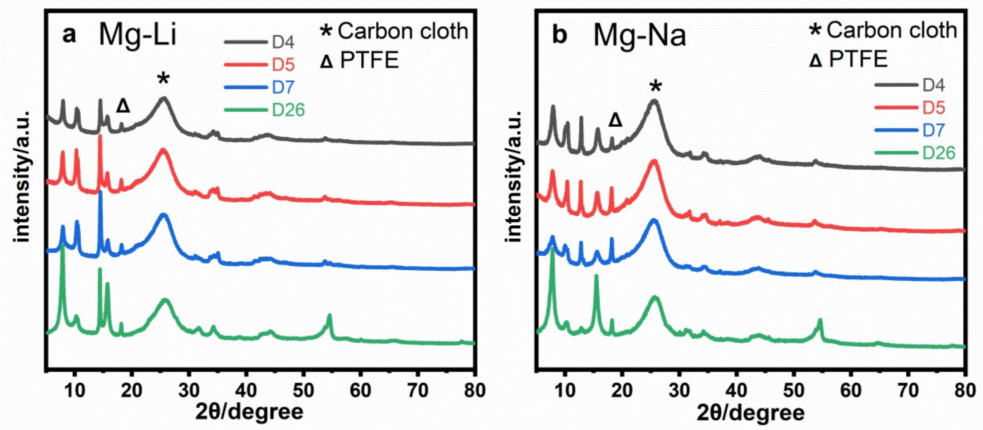

Fig. S5 Ex-situ XRD patterns of the discharged cathodes in (a) Mg^{2+}/Li^{+} and (b) Mg^{2+}/Na^{+} batteries at different cycles (50 mA g^{-1}).

References

[1] Z. Song, Z. Zhang, A. Du, S. Dong, G. Li and G. Cui, *Adv. Mater.*, 2021, *33*, 2100224.

[2] Z. Song, Z. Zhang, A. Du, S. Dong, G. Li and G. Cui, *J. Energy Chem.*, 2020, *48*, 299-307.