Supporting Information for

Monovalent vs Divalent Cation Diffusion in Thiospinel Ti$_2$S$_4$

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Experimental Methods

Material synthesis

Spinel CuTi$_2$S$_4$ was synthesized as explained elsewhere.$^{1-3}$ Briefly, inside an Ar-filled glove box, stoichiometric amounts of powders of the elements were mixed together and pressed into 12 mm diam. pellets totaling 1 g each, which were then cut in half and sealed inside an evacuated quartz tube (8 mm diameter, 12 cm long). The tube was heated at 1°C/min to 700°C, where it was held for 7 days before being cooled naturally and returned to the glove box where the powder product was removed from the tube, reground, re-pelletized and resealed back into a new tube. The tube was reheated to 700°C and held there for another 7 days. This second iteration improves the purity of the product CuTi$_2$S$_4$.

Cu$^+$ ions were removed by oxidizing CuTi$_2$S$_4$ in dry acetonitrile using twice the stoichiometric amount of Br$_2$ required and stirring the mixture in a sealed vial at room temperature for 3 days. The resulting Cu$_{0.1}$Ti$_2$S$_4$ particles ranged from 1 – 10 µm in diameter and were otherwise characterized previously.$^1$

Electrode fabrication

Inside an Ar-filled glove box, about 50 mg of Cu$_{0.1}$Ti$_2$S$_4$ powder was pressed at 6 tonnes in a 12 mm diameter pellet die to form the electrode. Sometimes, a 12 mm diameter, stainless steel 316, 150-size wire mesh was incorporated to help hold the pellet together and improve the conductivity of the pellet. Diffusion experiments performed on pellets without a wire mesh yielded the same results as one with a wire mesh, albeit with messier data and a more fragile pellet.

Cell fabrication

Conflat cells were designed by Periyapperuma et al.$^4$ and purchased from DPM Solutions Inc. (Design Prove Machine Solutions, Hebbville, NS, Canada). They were assembled inside an Ar-filled glove box using three layers of (dry) glass fiber filter paper as separators and either Mg or Li foil as the reference and counter electrodes. The electrolyte for the Li$_x$Ti$_2$S$_4$ cells was 1 M LiPF$_6$ in 1:1 EC:DMC, acquired from BASF.

Electrolyte synthesis

The electrolyte for Mg$_x$Ti$_2$S$_4$ cells was 0.5 M Mg(CB$_{11}$H$_{12}$)$_2$ in tetraglyme, made by Ka-Cheong Lau and Chen Liao of Argonne National Lab (ANL). A previously reported method was modified for the preparation of Mg(CB$_{11}$H$_{12}$)$_2$ in tetraglyme electrolyte.$^5$ A mixture of THF (5 mL), Mg powder (99.5%, 325 mesh; 3.99 g, 164 mmol), and [HNMe$_3$][CB$_{11}$H$_{12}$] (2.00 g, 9.85 mmol) were stirred at 60 °C for 1 h. After 1 h, additional THF (30 mL) was added to the reaction
mixture. A grey slurry was formed as the reaction proceeded. The reaction was monitored by \(^1\)H NMR of aliquots of the supernatant of the slurry, following the disappearance of Me\(_3\)NH\(^+\) resonance at \(\delta 3.19\) in acetone-\(d_6\). After completion, the slurry was filtered through a medium-porosity frit, and the solid was washed with THF. The solid was dissolved in DME (20 mL) to form a grey slurry, and the slurry was filtered through Celite on a medium-porosity frit to give a clear filtrate. The filtrate was collected and volatiles were removed at 60°C to give colorless to white crystals of [Mg(DME)\(_3\)](CB\(_{11}\)H\(_{12}\))\(_2\) (2.51 g, 4.32 mmol, 44 % yield). Anhydrous tetraglyme was added to [Mg(DME)\(_3\)](CB\(_{11}\)H\(_{12}\))\(_2\), and the mixture was stirred at room temperature for 12 h to form a clear solution of 0.5 M Mg(CB\(_{11}\)H\(_{12}\))\(_2\) in tetraglyme. Figure S1 shows a cyclic voltammogram (CV) of the electrolyte, demonstrating the plating and stripping behaviour.

![Cyclic voltammogram](image.png)

**Figure S1.** Cyclic voltammogram of Mg deposition and stripping from a solution of 0.5 M Mg(CB\(_{11}\)H\(_{12}\))\(_2\) in tetraglyme using a Pt working electrode, Mg counter electrode and Mg reference electrode at room temperature. The sweep rate was 100 mV/s.

**Electrochemical experiments**

*Galvanic Intermittent Titration Technique (GITT) and the Galvanic Alternating Pulse (GAP) technique*

The theory behind GITT experiments has been covered in detail by Weppner, Huggins and Wen, and interested readers are directed to their papers.\(^6\)–\(^8\) GAP is a GITT experiment where the polarity of the pulse is reversed each pulse so that the electrode is theoretically returned to the same state of charge after every second pulse. How to perform a GITT and GAP experiment, along with how to analyze the data, is covered by Talaie et al.\(^9\) and so will not be repeated here. We will, however, list the experimental parameters used in the GITT experiments that generated Figures 1 and 2 in the main text, as well as in the GAP experiments.
used to generate Figure 4 and the data in Table 1. For all cells, a Bio-logic VMP3 potentiostat was used to control the current and collect potential data from 3-electrode Conflat cells, employing pellet working electrodes (WE), foil reference and counter electrodes, separators and electrolyte as described above.

**GITT with Li₅Ti₂S₄ (Figures 1a and 2a):**

- Working electrode (WE) = 45.25 mg Ti₂S₄ pellet
- Data points were recorded every 10 mV or 10 s during current pulses
- Discharge at -240 μA (C/44) 0.5 h (Δx = 0.0228), OCV 4h, repeat until OCV < 2.4 V vs Li
- Discharge at -240 μA for 1.0 h (Δx = 0.0456), OCV 3 h, repeat until OCV < 1.88 V vs Li
- Discharge at -240 μA for 0.5 h, OCV 2 h, repeat until OCV < 1.80 V vs Li
- Charge at 240 μA for 0.5 h, OCV 2 h, repeat until OCV > 1.90 V vs Li
- Charge at 240 μA for 1.0 h, OCV 3 h, repeat until OCV > 2.40 V vs Li
- Charge at 240 μA for 0.5 h, OCV 2 h, repeat until OCV > 2.55 V vs Li
- Charge at 100 μA for 0.5 h, OCV 4 h, repeat until OCV > 2.65 V vs Li

**GITT with MgₓTi₂S₄ (Figures 1b and 2b):**

- Working electrode (WE) = 49.23 mg Ti₂S₄ pellet
- Data points were recorded every 10 mV or 10 s during current pulses
- Discharge at -150 μA (C/76) 2 h (Δx = 0.0262), OCV 4 h, repeat until OCV < 1.10 V vs Mg
- Discharge at -75 μA (C/150) 2 h (Δx = 0.0131), OCV 4 h, repeat until OCV < 0.90 V vs Mg
- Charge at 150 μA for 2.0 h, OCV 4 h, repeat until OCV > 1.50 V vs Mg
- Charge at 75 μA for 2.0 h, OCV 4 h, repeat until OCV > 1.62 V vs Mg

In the above details, small steps in x were used near the beginning and end of the V curve to probe the steeper slopes in these regions. The decision to use a shorter time or smaller current was based on the overpotential; the Li₅Ti₂S₄ pellet had a smaller overpotential, so there was no concern that the potential would rise to levels where the electrolyte would oxidize during charge pulses. This was not the case with the MgₓTi₂S₄ pellet, which had larger overpotentials and an electrolyte with a smaller electrochemical window. Hence, to avoid the potential descending low enough to plate Mg (< 0.1 V vs Mg) or high enough to oxidize the electrolyte (> 2.5 V vs Mg), the current was halved at the beginning and end of the V curve where the overpotentials were much larger than in the middle section.

To form Figure 1, the OCV at the end of each rest period was extracted and plotted vs x to form the quasi-equilibrium (so named because the OCV period ranged from 2 to 4 h instead of being infinite) voltage curves shown in Figure 1. Each individual pulse was then re-plotted on a V vs √t graph, beginning at t = 0. These new plots had linear sections in regions of
approximately $15 < \sqrt{t} < 25$ for $\text{Li}_x\text{Ti}_2\text{S}_4$, and $25 < \sqrt{t} < 35$ for $\text{Mg}_x\text{Ti}_2\text{S}_4$. The slope of these linear sections ($dV/d\sqrt{t}$) along with the slope of the equilibrium voltage curve ($dV/dx$, Figure 1) were used to calculate the self-diffusion coefficients for both $\text{Li}^+$ and $\text{Mg}^{2+}$ ($D_{\text{Li}}$ and $D_{\text{Mg}}$) as a function of $x$:

$$D_{\text{Mg}} \text{ or } D_{\text{Li}} = -\frac{4}{\pi} \left( \frac{kT}{Z_{\text{Mg}} \text{ or } Z_{\text{Li}} q e x} \right) \left( \frac{V_M}{nF S} \right) \left( \frac{l}{dV/d\sqrt{t}} \right)^2 \left( \frac{dV}{dx} \right).$$

This data was plotted in Figure 2.

**GAP Experimental Methods with $\text{Mg}_x\text{Ti}_2\text{S}_4$ (Figure 4 and Table 1):**

- Working electrode (WE) = 40 to 50 mg Ti$_2$S$_4$ pellets with a SS wire mesh
- Data points were collected every 10 mV or 5 s during each pulse and every 2 mV or 3 min during each OCV period
- Pulses lasted 30 min and OCV periods lasted 2.5 hours
- Current pulses: 90 μA, -90 μA, 120 μA, -120 μA, 150 μA, -150 μA, 180 μA, -180 μA, 210 μA and -210 μA
- Temperature was maintained with a Binder convection oven. The GAP experiment was repeated at 40, 50, 60, 70 and 80°C.

**GAP Experimental Methods with $\text{Li}_x\text{Ti}_2\text{S}_4$ (Table 1):**

- Working electrode (WE) = 90 to 100 mg Ti$_2$S$_4$ pellets
- Data points were collected every 10 mV or 5 s during each pulse and every 2 mV or 3 min during each OCV period
- Pulses lasted 30 min and OCV periods lasted 2 hours
- Current pulses: 90 μA, -90 μA, 120 μA, -120 μA, 210 μA, -210 μA, 240 μA and -240 μA
- Temperature was maintained with a Binder convection oven. The GAP experiment was repeated at 40, 50, 60, 70 and 80°C.

To form Figure 4, $dV/d\sqrt{t}$ was extracted from each current pulse and plotted vs the current. The slope of this plot ($dV/d\sqrt{t}/l$) was then used to calculate $D_{\text{Mg}} \text{ or } D_{\text{Li}}$ as per above, for a particular temperature. The oven temperature was then changed and the cell was allowed to reach equilibrium (i.e. the potential levelled out) before the next iteration of current pulses were initiated. Since the diffusion coefficient follows an Arrhenius dependence on temperature,$^9,10$

$$\ln D_{\text{Mg}} \text{ or } D_{\text{Li}} = -\frac{E_{\text{a,Diff}}}{kT} + \text{Constant},$$

S5
a plot of $\ln(D_{\text{Mg or Li}})$ vs $1/T$ should yield a straight line where $E_{a,\text{Diff}}$ can be extracted from the slope.

**Supplementary Figures**

**Figure S2.** Pictures of Mg dendrites taken during cell disassembly. (A) Dendrites passing through all three layers of glass fiber filter paper separator used in the Conflat, 3-electrode cells. (B) Evidence that Celgard microporous separator did not stop the growth of dendrites. This picture shows a torn piece of glass fiber filter paper separator still attached by Mg dendrites to a Celgard 3501 separator, which is still attached to the Mg foil disk below it. The electrolyte was 0.5 M Mg(CB$_{11}$H$_{12}$)$_2$ in tetraglyme and the current was 130 μA/cm$^2$.

**Figure S3.** Extrapolation of Arrhenius data for Li$_x$Ti$_2$S$_4$/Li and Mg$_x$Ti$_2$S$_4$/Mg cells down to 25°C. a) Chemical diffusion coefficients. b) Self-diffusion coefficients. Recall $D^C = W/D$, where $W = \text{thermodynamic factor.}^6$ Mg ions appear to diffuse 100 to 1000 times slower at room temperature than Li ions in Ti$_2$S$_4$. 

References


