# Superfast High-Energy Storage Hybrid Device Composed of MXene and Chevrel Phase Electrodes Operated in Saturated LiCl Electrolyte Solution

Fyodor Malchik<sup>a</sup>, Netanel Shpigel<sup>a</sup>, Mikhael D Levi<sup>a</sup>, Tyler S. Mathis<sup>b</sup>, Albert Mor<sup>a</sup>, Yury Gogotsi<sup>b</sup>, and Doron Aurbach<sup>\*a</sup>

## **Supporting information**

#### Experimental

#### Materials synthesis and characterization

**Chevrel phase** (Mo<sub>6</sub>S<sub>8</sub>) powder was synthesized via solid state reaction under annealing of a well-homogenized stoichiometric mixture of CuS, MoS<sub>2</sub> and Mo powders (2:3:3 molar ratio) following the procedure reported elsewhere<sup>1</sup>. The mixed powder was pressed 3 times into pellet by a tablet pressing machine (P = 5 ton/m2) into compact disks and annealed in a Swagelock autoclave under Ar flow (900 °C, 24 h) to form Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> phase powder. The obtained Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> was leached in 6 M HCl under oxygen bubbling and continuous stirring during 6 h. Afterwards, the leached powder was dried overnight under vacuum at 80 °C.

 $Ti_3C_2$  was synthesized from 1 g  $Ti_3AIC_2$  powder immersed in an etchant mixture containing 20 mL HCl (9M) + (1 g) LiF<sup>2</sup>. The colloidal suspension formed after 24h continuous stirring at 35°C was washed by centrifugation in deionized water until a supernatant with a pH value of ~6 was obtained.

YP-50 was purchased from Kuraray, Japan. BET surface area of 1693m<sup>2</sup>/g<sup>3</sup>, 5μm average particle size.

#### Free-standing electrode preparation and electrochemical measurements

Weighed amount of Chevrel phase powder was added to a 16 ml of aqueous slurry (with concentration of 4.3 g/mL). for better homogenization, the suspension was mixed by probe sonicator for 10 min. The obtained dispersion was vacuum filtered through a PVdF membrane (47mm diameter, Millipore) and then dried overnight under vacuum. The dry film was peeled off the membrane to get a free-standing film, and then punched into 6mm circles. The mass of the obtained circular electrodes having different MXene/Chevrel mass ratio was measured by accurate electric micro balance ( $\pm 10 \mu g$  detecting limit) and found to be 300  $\mu g$  to 570  $\mu g$  for the neat MXene compound and the 50% hybrid electrode respectively.

The electrochemical measurement was done using a T-cell configuration using glassy carbon electrodes as current collectors, activated carbon, and Ag/AgCl as counter and reference electrodes, respectively.

**Electrochemical impedance spectroscopy (EIS)** measurement was done in 3 electrode cell in which 20 uL of MXene suspension was coated directly on glassy carbon electrode and dry for 1 h. Grafoil counter electrode was placed in a constant distance from the working MXene electrode and Ag/AgCl reference was located in close proximity (0.5 mm) to the working electrode. The EIS was conducted in the frequency range from 200 kHz to 20 mHz at OCV applying a voltage amplitude of 10 mV.

Calculations of the specific capacitance for the hybrid system, was done in a 3-electrode configuration according to the following formula:

$$C_g = \frac{i}{m\nu} \tag{1}$$

Where *i* is the current density, *t* is the time, *m* is the working electrode mass, v is the scan rate (mV/s) and *V* is the applied potential window.

The specific gravimetric energy and power density of the hybrid system was calculated using the following equation:

$$E_g = \frac{1}{m} \int iEdt = \frac{1}{m} \int Edq \tag{2}$$

$$P_g = \frac{E_g}{\Delta t} \tag{3}$$

Where q, E and t are charge, potential, and time, respectively.

#### Instrumentation

**HR-SEM** imaging was performed using Magellan XHR 400L FE-SEM (FEI Company) equipped by EDS detector (oxford instruments).

**XRD studies** were conducted with a Bruker Inc. (Germany) AXS D8 ADVANCE diffractometer (reflection y–y geometry; Cu Ka radiation, Ni-filter; scintillation counter).

In situ EQCM-D measurements were done by QSense E1 module (QCM-D from Biolin Scientific) on 5 MHz Au-coated QCM sensor (q-sense Scientific AB, Swedenusing). The quartz sensor first coated by MXene (mass change of 17.66 µg/cm<sup>2</sup>) and then coated by a second layer of Chevrel (mass change of 14.13 µg/cm<sup>2</sup>) to get a thin hybrid electrode film. The coated sensor (operates as a working electrode) was assembled in a home designed 3 electrode cell using grafoil disk as a counter electrode and Ag/AgCl/KCl (sat.) as a reference electrode. electrochemical measurements were conducted by BioLogic VSP-300 with EC-Lab software.

**4-point probe conductivity measurements** were performed on free-standing MXene films at 5 different locations, using a Keithley 2410 system equipped with 4-probe station with a probe spacing of 2.3 mm

# Supplementary figures



Figure S1 SEM image (1  $\mu m$  scale) and XRD patterns of pristine  $Mo_6S_8$  particles



**Figure S2** Cyclic voltammograms obtained at 1 mV/s and 10 mV/s for 70% Chevrel phase loaded hybrid electrodes (where *I* is the current, *v* denotes scan rate and *m* is mass of the electrode).



**Figure S3** Cyclic voltammograms obtained at different scan rates (as indicated) for pure Chevrel phase electrodes (where *I* is the current, *v* denotes scan rate and *m* is mass of the electrode)



Figure S4: SEM image of YP-50 activated carbon which was used as a positive electrode for the hybrid MXene/Chevrel system



Figure S5 Cyclic voltammograms of activated carbon (YP-50) and hybrid MXene/Chevrel phase electrodes measured individually at 3 electrodes system in saturated LiCl. Scan rate 25 mV/s.



**Figure S6** Example of the use of the integral formulas for the calculation of specific energy,  $E_g$ , for the ideal capacitive and battery-type behaviors (Eqs. (3) and (4), for Ti<sub>3</sub>C<sub>2</sub> and Mo<sub>6</sub>S<sub>8</sub>, respectively). The specific energy for the Ti<sub>3</sub>C<sub>2</sub> component of the hybrid electrode is represented by the sum of the surface areas of the red dashed triangular and rectangular whereas the energy of Mo<sub>6</sub>S<sub>8</sub> component is represented by the sum of the surface areas of two black dashed rectangular. The specific energies of Ti<sub>3</sub>C<sub>2</sub> and Mo<sub>6</sub>S<sub>8</sub> (referred to the mass of hybrid electrodes) were found to be 12.1 and 30.0 Wh/kg, virtually the same as that obtained by the numerical integration, 12.0 and 30.3 Wh/kg, respectively. The integral formulas (3) and (4) cannot be applied to treat the voltage profile of the hybrid electrode

since it reveals mixed battery-capacitor behavior. In contrast, numerical integration of this curve provides accurate result of integration in this case.

•



Figure S7 Long term cycling performance and cycling efficiency obtained for the neat compounds at 50mV/s



Figure S8 The CV responses recorded at different scan rates used for the calculation of the hybrid electrodes' kinetic coefficients (listed in Table S2).



Figure S9. Current versus scan rate dependences (in double log coordinates) calculated with the slopes found from fitting the experimental points for the hybrid Chevrel phase/Mxene electrode (the slopes indicated in Fig. 9) within the pseudo-capacitive, diffusion and capacitive domains (dashed lines of different colours as indicated). The calculated current using in-series-parallel combination is shown by solid red line. The experimental points are shown



by open red circles.

**Figure 10** Current versus scan rate dependences (in double log coordinates) calculated using in-series-parallel combination of the current in pseudo, diffusion and capacitive domains using Eq. (7) (solid black line). The dashed lines are the limiting slopes of all three domains. For the pseudo, diffusion and capacitive domains the proportionality constant, *a*, and the slope, *b*, were assumed to be: (0.89 and -2.586), (0.50 and -3.334), (0.88 and -4.900), respectively.



**Figure S11.** Frequency and dissipations signals recorded for 1<sup>st</sup>,3<sup>rd</sup> and 5<sup>th</sup> overtones during potential scanning at 5mV/s. The negligible dissipation changes (appear as dashed lines) followed by overtone dependent response imply on pure gravimetric response.

**Table S1** . Specific capacities, energy and power densities of neat Chevrel and MXene, and the hybrid Chevrel/MXeneelectrode (30% Chevrel) tested at 1 and 1000 mV/s (the data relate to Fig. 8d, e)

v (mV/s)	1		
Characteristics	C(mAh/g)	W (Wh/kg)	P(W/kg)
Neat Chevrel	89.5	65.3	2.24×10 <sup>2</sup>
Hybrid 30% Chevrel	63.8	46.3	1.15×10 <sup>2</sup>
MXene	44.4	32.3	80.0
v (mV/s)	1000		
Characteristic	C(mAh/g)	W (Wh/kg)	P(W/kg)
Neat Chevrel	10.8	7.9	2.71×10 <sup>4</sup>

	ν (mV/s)	b	а
Pure Mxene	0.1-1000	1	-3.62
Pure Chevrel	0.1-1	0.9	-2.81
	5-1000	0.54	-3.87
Hybrid Mxene/Chevrel	0.1-1	0.9	-2.58
	2.5-75	0.63	-3.33
	500-1000	0.88	-3.12
Hybrid 30% Chevrel	21.9	15.9	3.94×10 <sup>4</sup>
MXene	23.7	17.2	4.27×10 <sup>4</sup>

**Table S2.** The obtained values of *a* and *b* parameters in the related range of the scan rates as found for the pure and the hybrid systems.

## References

- 1. Gershinsky, G. *et al.* Ultra fast elemental synthesis of high yield copper Chevrel phase with high electrochemical performance. *J. Solid State Chem.* **188**, 50–58 (2012).
- 2. Zhang, T. *et al.* Synthesis of two-dimensional Ti3C2Tx MXene using HCl+LiF etchant: Enhanced exfoliation and delamination. *J. Alloys Compd.* **695**, 818–826 (2017).
- 3. Zhang, C. *et al.* Highly porous carbon spheres for electrochemical capacitors and capacitive flowable suspension electrodes. *Carbon N. Y.* **77**, 155–164 (2014).