

## MXene as Charge Storage Host

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## Methods

MXenes were prepared by the literature methods.<sup>1,2</sup>

**Material characterization.** Hard X-ray photoelectron spectra (HXPES) measurements were performed using synchrotron radiation on beamline BL46XU of SPring-8. The excitation energy used for HXPES was 7853 eV. The X-ray absorption spectroscopy was conducted in the transmission mode at room temperature at BL-9C of Photon Factory. The DC magnetic susceptibility was measured by a Quantum Design MPMS-5S SQUID susceptometer in the temperature range from 5 to 300 K with a field of 0.1 T. The magnetic susceptibility was corrected for the core diamagnetism estimated from Pascal's constants.

**Electrochemical measurement.** For the electrochemical measurements in aqueous electrolytes, the working electrode was fabricated by mixing MXene, acetylene black and polytetrafluoroethylene in 80:10:10 weight ratio. The resulting paste was pressed onto a nickel mesh. A three-electrode glass cell was assembled with a Pt mesh as the counter electrode, Ag/AgCl in saturated aqueous solution of KCl for a reference electrode and 0.5 M aqueous solutions of Li<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub> for the electrolyte. The sweep rate of the cyclic voltammetry (CV) measurements was set to 0.5 mV s<sup>-1</sup>, and the cut-off voltages were -0.7 V and -0.1 V (vs. Ag/AgCl). The specific capacitance from the CV curve was calculated as  $\frac{1}{\Delta V} \int \frac{j(V)}{s} dV$ , where  $V$  is the potential,  $\Delta V$  is the potential window,  $j(V)$  is the specific current, and  $s$  is the scan rate.

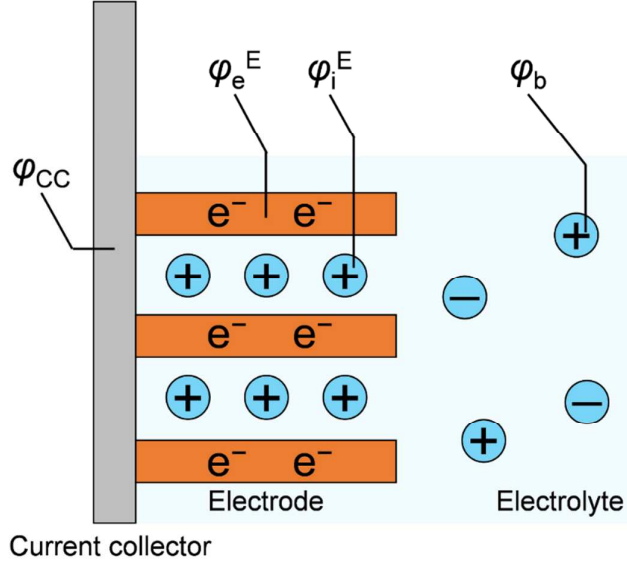


Figure S1. Schematic illustration of an electrode that stores cations. The inner potentials of the current collector, the electrode, the stored cations, and the bulk electrolyte are  $\varphi_{CC}$ ,  $\varphi_e^E$ ,  $\varphi_i^E$ , and  $\varphi_b$ , respectively.

The specific capacitance ( $C$ ) of an electrode in Figure S1 is defined as  $C = \frac{\Delta Q}{\Delta(\varphi_{CC} - \varphi_b)}$ , where  $\Delta(\varphi_{CC} - \varphi_b)$  is the change of the inner potential difference between a current collector ( $\varphi_{CC}$ ) and a bulk electrolyte ( $\varphi_b$ ), and  $\Delta Q$  is a stored charge per the weight of the electrode. Note that  $\Delta(\varphi_{CC} - \varphi_b)$  is equivalent to the voltage change of the electrode versus a reference electrode.

$\varphi_{CC} - \varphi_b$  is expanded by the inner potential differences as,

$$\varphi_{CC} - \varphi_b = (\varphi_{CC} - \varphi_e^E) + (\varphi_e^E - \varphi_i^E) + (\varphi_i^E - \varphi_b).$$

The equilibrium condition of the electron electrochemical potential  $\eta_e$  between the current collector and the electrode applies to give,

$$\eta_e^{CC} = \eta_e^E,$$

which leads to,

$$\mu_e^{CC} - F\varphi_{CC} = \mu_e^E - F\varphi_e^E.$$

The equilibrium condition of the ion electrochemical potential  $\eta_i$  between the electrode and the electrolyte also applies to give,

$$\eta_i^E = \eta_i^b,$$

which leads to,

$$\mu_i^E + F\phi_i^E = \mu_i^b + F\phi_b.$$

Therefore,

$$\phi_{CC} - \phi_b = \frac{\mu_e^{CC} - \mu_e^E}{F} + (\phi_e^E - \phi_i^E) + \frac{\mu_i^b - \mu_i^E}{F}$$

Because  $\mu_e^{CC}$  and  $\mu_i^b$  is constant during charge/discharge processes,  $\Delta(\phi_{CC} - \phi_b)$  is expressed as,

$$\Delta(\phi_{CC} - \phi_b) = \Delta(\phi_e^E - \phi_i^E) - \frac{\Delta(\mu_e^E + \mu_i^E)}{F}$$

If the density of states of the electrode is significantly large relative to the amount of the stored electron,  $\mu_e^E$  is almost constant during the charge/discharge processes to give  $\Delta\mu_e^E = 0$ . In addition, if the number of the site for cation storage in the electrode is significantly large relative to the amount of the stored cation,  $\mu_i^E$  is almost constant during the charge/discharge processes to give  $\Delta\mu_i^E = 0$ . Therefore,  $\Delta(\phi_{CC} - \phi_b) = \Delta(\phi_e^E - \phi_i^E)$  applies for small  $\Delta Q$  (e.g., charging/discharging MXene in aqueous electrolytes), and the electrode behaves as an EDL capacitor.

Conversely, when the electrode is charged/discharged with organic electrolytes, desolvated bare cations are intercalated to induce orbital hybridization with surface termination groups (charge transfer). The charge transfer strongly screens the electric field between the electron and the cation, leading to suppress  $\Delta(\phi_e^E - \phi_i^E)$ . More importantly, owing to the wide potential window of the organic electrolytes, a large amount of electron and cation is stored upon charge, leading to the considerable changes of  $\mu_e^E$  and  $\mu_i^E$  due to band filling effect and inter-cation interaction. In this situation, the electrode behaves as a pseudocapacitor to deliver a pseudocapacitance (or redox/quantum/chemical capacitance). For the limiting case where the electric field within the electrode is completely screened by sufficient charge transfer and the inner potential is uniform ( $\phi_e^E$

$= \varphi_i^E$ ), the applied potential difference is described only by the chemical potentials of electron and ion (Nernst equation).

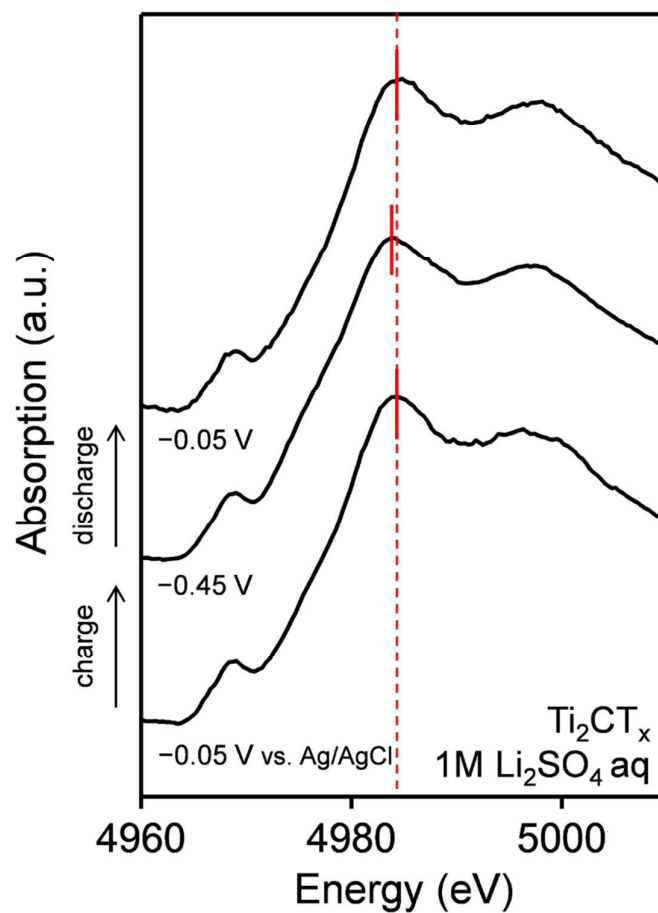


Figure S2. X-ray absorption spectra of  $\text{Ti}_2\text{CT}_x$  in a  $1\text{M Li}_2\text{SO}_4$  aqueous electrolyte upon charge/discharge. The peak top position of a main edge slightly shifts to a lower energy side after the charge while it returns to the initial position after the discharge, which indicates the reversible redox reaction of Ti.

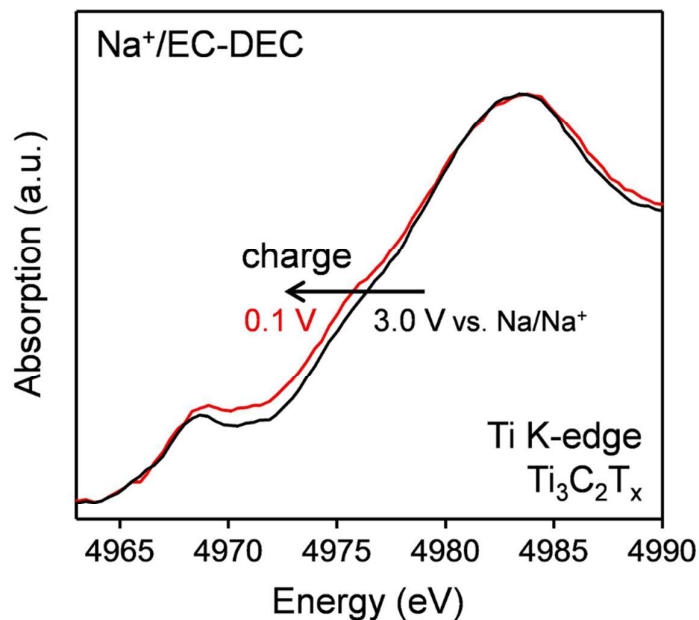


Figure S3. X-ray absorption spectra of  $\text{Ti}_3\text{C}_2\text{T}_x$  in a 1 M  $\text{NaPF}_6$  / ethylene carbonate (EC)-diethyl carbonate (DEC) electrolyte before and after charge.<sup>2</sup> Upon charge, whereas the peak top position of a main edge does not shift, absorption increases at an energy region around 4975 eV, presumably owing to the slight reduction of Ti. Because the charge transfer between the larger  $2s$  orbital of  $\text{Na}^+$  and surface termination groups is larger than that with  $\text{Li}^+$ , stored electron may reside near the surface termination groups (see text).

## References

1. Kajiyama, S.; Szabova, L.; Iinuma, H.; Sugahara, A.; Gotoh, K.; Sodeyama, K.; Tateyama, Y.; Okubo, M.; Yamada, A. Enhanced Li-Ion Accessibility in MXene Titanium Carbide by Steric Chloride Termination. *Adv. Energy Mater.* **2017**, *7*, 1601873.
2. Kajiyama, S.; Szabova, L.; Sodeyama, K.; Iinuma, H.; Morita, R.; Gotoh, K.; Tateyama, Y.; Okubo, M.; Yamada, A. Sodium-Ion Intercalation Mechanism in MXene Nanosheets. *ACS Nano* **2016**, *10*, 3334-3341.