SUPPORTING INFORMATION:

A. Synthesis and Structural/Compositional Analysis of WO_3 Thin Films

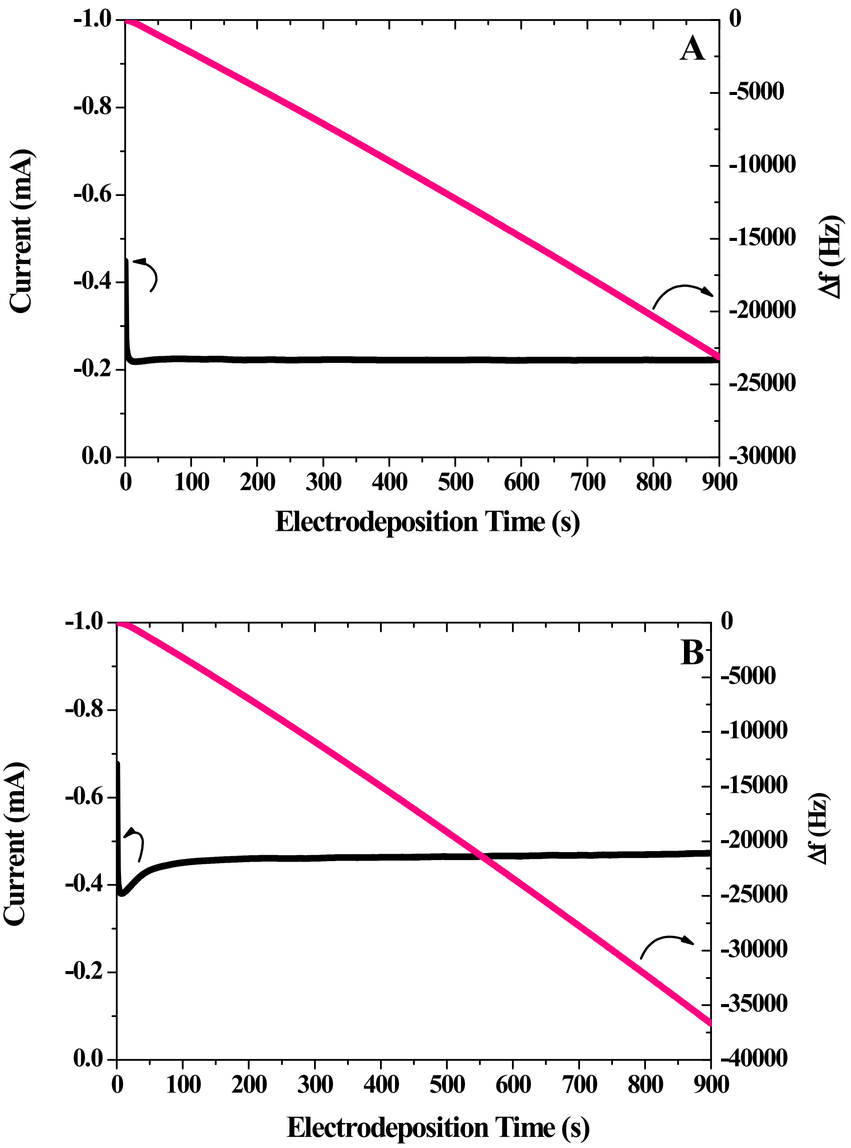

Figure S1. Typical electropotentiostatic deposition data and simultaneous QCM characterization (frequency variation of the quartz crystal during electrodeposition) of **A.** dense and **B.** mesoporous WO_3 thin films.

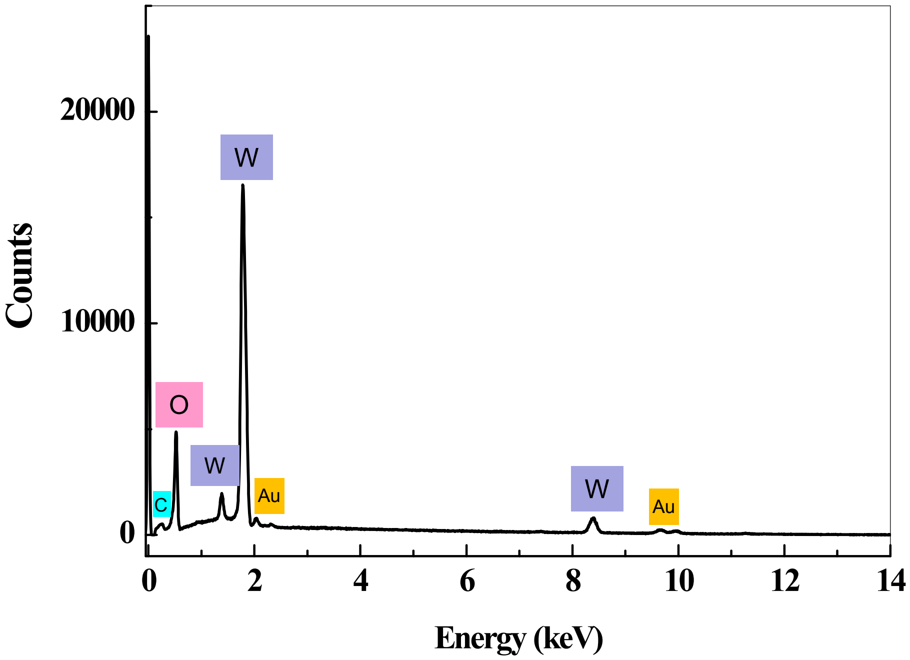

Fig. S2 Compositional analysis by energy dispersive X-ray (EDX) spectroscopy of a dense WO_3 thin film (obtained by FEG-SEM equipped with an EDX detector) (substrate: gold electrode of the quartz resonator).

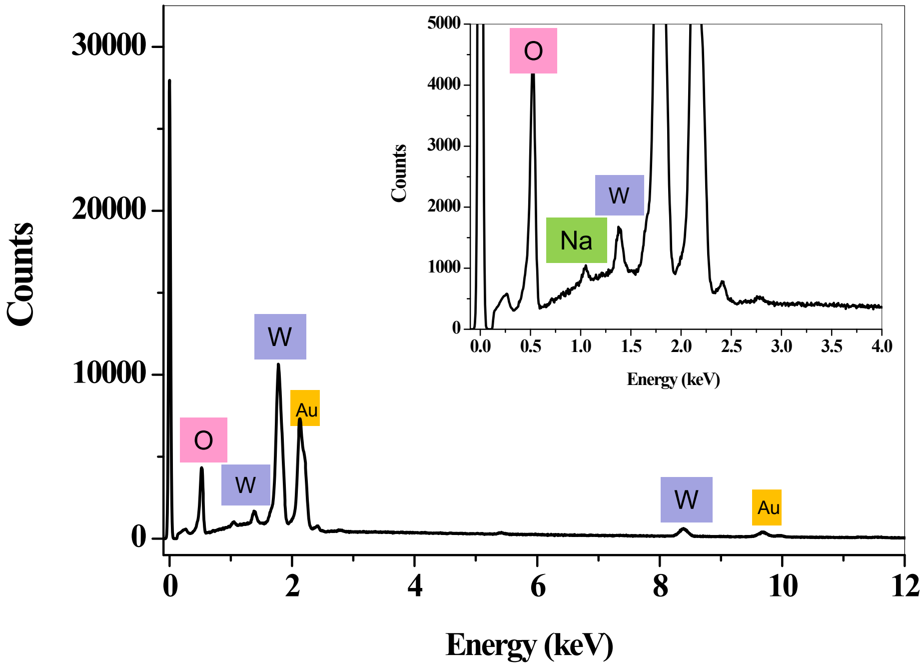

Fig. S3 Compositional analysis by energy dispersive X-ray (EDX) spectroscopy of an inorganic/organic hybrid WO_3 thin film before the removal of the SDS surfactant (obtained by FEG-SEM equipped with an EDX detector) (substrate: gold electrode of the quartz resonator).

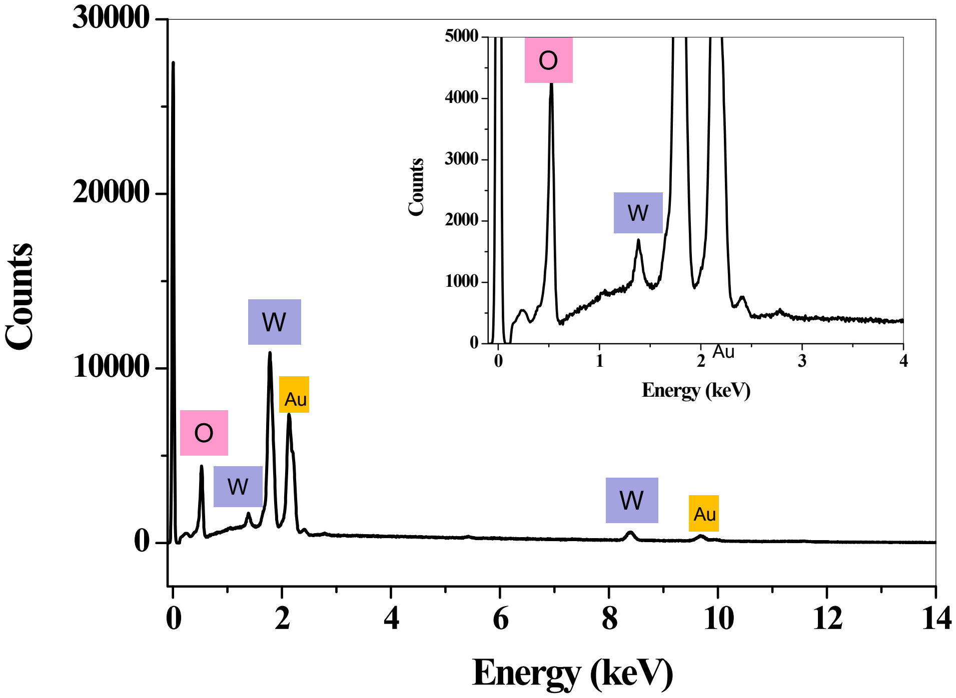

Fig. S4 Compositional analysis by energy dispersive X-ray (EDX) spectroscopy of a mesoporous WO_3 thin film after the removal of the SDS surfactant (obtained by FEG-SEM equipped with an EDX detector) (substrate: gold electrode of the quartz resonator).

B. Theoretical Model with three different sites in WO_3 thin films associated to two cations c1 and c2, and an anion a:

(i) Electrochemical reactions and kinetics

The transfer of two cations ($\mathrm{c1}$ and $\mathrm{c2}$), and an anion (a) in the electroactive films incorporating three different sites, $\mathrm{P1, P2}$, and $\mathrm{P3}$ during the redox reaction of the host material $\langle \mathrm{P} \rangle$ where a single electronic transfer takes place in three independent sites can be expressed as:

$$\langle \mathrm{P1} \rangle + \mathrm{e}^- + \mathrm{c1}^+ \underset{\mathrm{k}'_{\mathrm{c1}}}{\overset{\mathrm{k}_{\mathrm{c1}}}{\rightleftarrows}} \langle \mathrm{P1c1} \rangle \tag{1}$$

$$\langle \mathrm{P2} \rangle + \mathrm{e}^- + \mathrm{c2}^+ \underset{\mathrm{k}'_{\mathrm{c2}}}{\overset{\mathrm{k}_{\mathrm{c2}}}{\rightleftarrows}} \langle \mathrm{P2c2} \rangle \tag{2}$$

$$\langle \mathrm{P3} \rangle + \mathrm{a}^- \underset{\mathrm{k}'_{3}}{\overset{\mathrm{k}_{3}}{\rightleftarrows}} \langle \mathrm{P3a} \rangle + \mathrm{e}^- \tag{3}$$

where $\langle \mathrm{P1c1} \rangle$ and $\langle \mathrm{P2c2} \rangle$ are the film matrices doped with cations, and $\langle \mathrm{P3a} \rangle$ is the film matrices doped with anions. The cation and anion transfers at the film|solution interface are only taken into account as rate-limiting steps since the ionic transports inside the thin film and in the solution are supposed to be fast enough through thin films or in sufficiently concentrated electrolytes.

The net instantaneous molar flux change of each cations, ΔJ_{c1} and ΔJ_{c2}, can be written as follows taking into account the various concentrations and kinetic rate of transfer:

$$J_{c1}(d_f) = -d_f \frac{dC_{c1}}{dt} = k'_{c1}\left(C_{c1} - C_{c1\min}\right) - k_{c1}\left(C_{c1\max} - C_{c1}\right)C_{c1sol} \tag{4}$$

$$J_{c2}(d_f) = -d_f \frac{dC_{c2}}{dt} = k'_{c2}\left(C_{c2} - C_{c2\min}\right) - k_{c2}\left(C_{c2\max} - C_{c2}\right)C_{c2sol} \tag{5}$$

$$J_{a}(d_f) = -d_f \frac{dC_{a}}{dt} = k_{a}\left(C_{a} - C_{a\min}\right) - k'_{a}\left(C_{a\max} - C_{a}\right)C_{asol} \tag{6}$$

By using the Hillman solvation model [A. Jackson, A. R. Hillman, S. Bruckenstein, I. Jureviciute, J. Electroanal. Chem., 524 (2002) 90] the same relationship can be used for the solvent flux:

$$J_{s}(d_f) = -d_f \frac{dC_{s}}{dt} = k'_{s}\left(C_{s} - C_{s\min}\right) - k_{s}\left(C_{s\max} - C_{s}\right) \tag{7}$$

where (α) d_f is the film thickness; (β) C_i is the concentration of species i in the film, C_{isol} is the concentration of species i in the solution by assuming that the diffusion of the ions in solution does not limit the global kinetics; (χ) the term ($C_{imax} - C_i$) is the concentration in free sites for species i at time t, where C_{imax} is the maximum concentration of the free sites in the film for species i; (δ) the term ($C_i - C_{imin}$) is the concentration of species i in the film bulk at time t, where C_{imin} is the minimum concentration of species i in the film.

The kinetic constants which appear here depend on the potential under the classical form:

$$k_i^{'} = k_{i_0}^{'} e^{\left[b_i^{'}\left(E-E_i^o\right)\right]} \tag{8}$$

$$k_i = k_{i_o} e^{\left[b_i\left(E-E_i^o\right)\right]} \tag{9}$$

where E is the potential, E_i° is the apparent normal potential, (E- E_i°) is the overvoltage, k_{i0}, k'_{i0}, b_{i0} and b'_{i0} are constants.

(ii) Dynamic regime and flux of each species

Under the effect of a sinusoidal potential perturbation with low amplitude, ΔE, imposed to the electrode/film/electrolyte system, sinusoidal fluctuations of concentration, ΔC_i, and flux, ΔJ_i, are observed such as:

$$\Delta J_i = -d_f \frac{dC_i}{dt} = -j\omega d_f \Delta C_i \tag{10}$$

The expression of the global insertion/expulsion flux, ΔJ_i, which depends on the concentration and potential perturbations, at the film/electrolyte interface is:

$$\Delta J_i = \left.\frac{\partial J_i}{\partial C_i}\right)_E \Delta C_i + \left.\frac{\partial J_i}{\partial E}\right)_{C_i} \Delta E = K_i \Delta C_i(d_f) + G_i \Delta E \tag{11}$$

where $j = \sqrt{-1}$, $\omega = 2\pi f$ is the pulsation, f is the perturbation frequency and K_i and G_i are the partial derivatives of the flux, J_i, with respect to the concentration and the potential respectively, $K_i = \left(\frac{\partial J_i}{\partial C_i}\right)_E$ and $G_i = \left(\frac{\partial J_i}{\partial E}\right)_{C_i}$, where J_i stands for the flux of the species i crossing the film/electrolyte interface. More precisely, K_i is the kinetics rate of transfer and G_i is the inverse of the transfer resistance, Rt_i, of the species at the film/electrolyte interface (where i is the cation c1, cation c2, anion a, or the free solvent s). Therefore, the characteristic frequency, f_i, of the transfer can be estimated through the following equation:

$$f_i = \frac{K_i}{\pi d_f} \tag{12}$$

The transfer resistance, Rt_i, can be calculated taking into account the values of G_i:

$$Rt_i = \frac{1}{FG_i} \tag{13}$$

For each transferred species, the ionic transfer resistance, Rt_i, is a good estimation of the ease of the transfer.

(iii) Charge/ potential transfer function, $\left.\frac{\Delta q}{\Delta E}\right|_{th}$

The charge/potential transfer function, $\left.\frac{\Delta \mathrm{q}}{\Delta \mathrm{E}}\right|_{\mathrm{th}}$, is calculated for the insertion/expulsion of the two cations, *c1* and *c2* and an anion, *a* and by using the Faraday number, F, and the film thickness, d_f:

$$\left.\frac{\Delta q}{\Delta E}\right|_{th}(\omega) = -Fd_f\left(\left.\frac{\Delta C_{c1}}{\Delta E}\right|_{th} + \left.\frac{\Delta C_{c2}}{\Delta E}\right|_{th} - \left.\frac{\Delta C_a}{\Delta E}\right|_{th}\right) \tag{14}$$

Then, for the two cations, c1 and c2, and an anion it comes:

$$\left.\frac{\Delta q}{\Delta E}\right|_{th}(\omega) = Fd_f\left(\frac{G_{c1}}{j\omega d_f + K_{c1}} + \frac{G_{c2}}{j\omega d_f + K_{c2}} - \frac{G_a}{j\omega d_f + K_a}\right) \tag{15}$$

(iv) Electrochemical impedance, $\left.\frac{\Delta E}{\Delta I}\right|_{th}$

Then, the Faradaic impedance, $Z_F(\omega)$ relative to the global ionic transfer of the electroactive film for three charged species, cations (c1 and c2) and anion involved in the charge compensation is:

$$\left.Z_F\right|_{th}(\omega) = \left.\frac{\Delta E}{\Delta I_F}\right|_{th}(\omega) = \frac{1}{j\omega\left.\frac{\Delta q}{\Delta E}\right|_{th}(\omega)} \tag{16}$$

And using Eq. (15), we can obtain for the Faradaic impedance, Z_F:

$$\left.Z_F\right|_{th}(\omega) = \left.\frac{\Delta E}{\Delta I_F}\right|_{th}(\omega) = \frac{1}{j\omega d_f F\left[\frac{G_{c1}}{(j\omega d_f) + K_{c1}} + \frac{G_{c2}}{(j\omega d_f) + K_{c2}} - \frac{G_a}{(j\omega d_f) + K_a}\right]} \tag{17}$$

Finally, the electrochemical impedance can be estimated incorporating the electrolyte resistance, R_{el} and the interfacial capacitance, C_{dl}:

$$\left.\frac{\Delta E}{\Delta I}\right|_{th}(\omega) = R_{el} + \frac{1}{j\omega C_{dl} + \frac{1}{\left.Z_F\right|_{th}(\omega)}} \tag{18}$$

or with the K_i and G_i parameters related to the two cations and an anion:

$$\left.\frac{\Delta E}{\Delta I}\right|_{th}(\omega) = R_{el} + \frac{1}{j\omega C_{dl} + j\omega d_f F j\omega d_f F\left[\frac{G_{c1}}{(j\omega d_f) + K_{c1}} + \frac{G_{c2}}{(j\omega d_f) + K_{c2}} - \frac{G_a}{(j\omega d_f) + K_a}\right]} \tag{19}$$

When the response of the electrochemical system is perturbed at low frequencies with a parasitic electrochemical reaction, characterized by a parasitic impedance ($Z_{par}(\omega)$) described in equation (20), in parallel with the ionic transfer, the global electrochemical impedance becomes as shown in equation 21.

$$Z_{par}(\omega) = R_{par} + \frac{1}{j\omega C_{par}} \tag{20}$$

$$\frac{\Delta E}{\Delta I}(\omega) = R_{el} + \frac{1}{j\omega C_{dl} + \left.\frac{\Delta I}{\Delta E}\right)_{ions}(\omega) + \frac{1}{Z_{par}(\omega)}} \tag{21}$$

(v) Mass/potential transfer function, $\left.\frac{\Delta m}{\Delta E}\right|_{th}(\omega)$

The electrogravimetric transfer function, $\left.\frac{\Delta m}{\Delta E}\right|_{th}(\omega)$, can be calculated theoretically, taking into account of the uncharged species contribution (solvent molecules in this case) through the two parameters K_s and G_s:

$$\left.\frac{\Delta m}{\Delta E}\right|_{th}(\omega) = -d_f\left(m_{c1}\frac{G_{c1}}{(j\omega d_f) + K_{c1}} + m_{c2}\frac{G_{c2}}{(j\omega d_f) + K_{c2}} + m_a\frac{G_a}{(j\omega d_f) + K_a} + m_s\frac{G_s}{(j\omega d_f) + K_s}\right) \quad (2$$

2)

where m_{c1}, m_{c2}, m_a and m_s are the atomic weight of involved species.

Partial mass/potential TF are also estimated either by removing the c2 contribution, calculating $\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c1as}(\omega)$; or the c1 contribution, calculating $\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c2as}(\omega)$; or the anion contribution, calculating $\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c1c2s}(\omega)$ .The following equations are used:

In the case of the cation c1, anion and the solvent:

$$\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c1as}(\omega)=d_f\left((m_{c1}-m_{c2})\frac{\Delta C_{c1}}{\Delta E}+(m_a+m_{c2})\frac{\Delta C_a}{\Delta E}+m_s\frac{\Delta C_s}{\Delta E}\right) \tag{23}$$

In the case of the cation c2, anion and the solvent:

$$\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c2as}(\omega)=d_f\left((m_{c2}-m_{c1})\frac{\Delta C_{c2}}{\Delta E}+(m_a+m_{c1})\frac{\Delta C_a}{\Delta E}+m_s\frac{\Delta C_s}{\Delta E}\right) \tag{24}$$

In the case of the cation c1, cation c2, and the solvent:

$$\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c1c2s}(\omega)=d_f\left((m_{c1}+m_a)\frac{\Delta C_{c1}}{\Delta E}+(m_{c2}+m_a)\frac{\Delta C_2}{\Delta E}+m_s\frac{\Delta C_s}{\Delta E}\right) \tag{25}$$

C. Partial Electrogravimetric Transfer Functions:

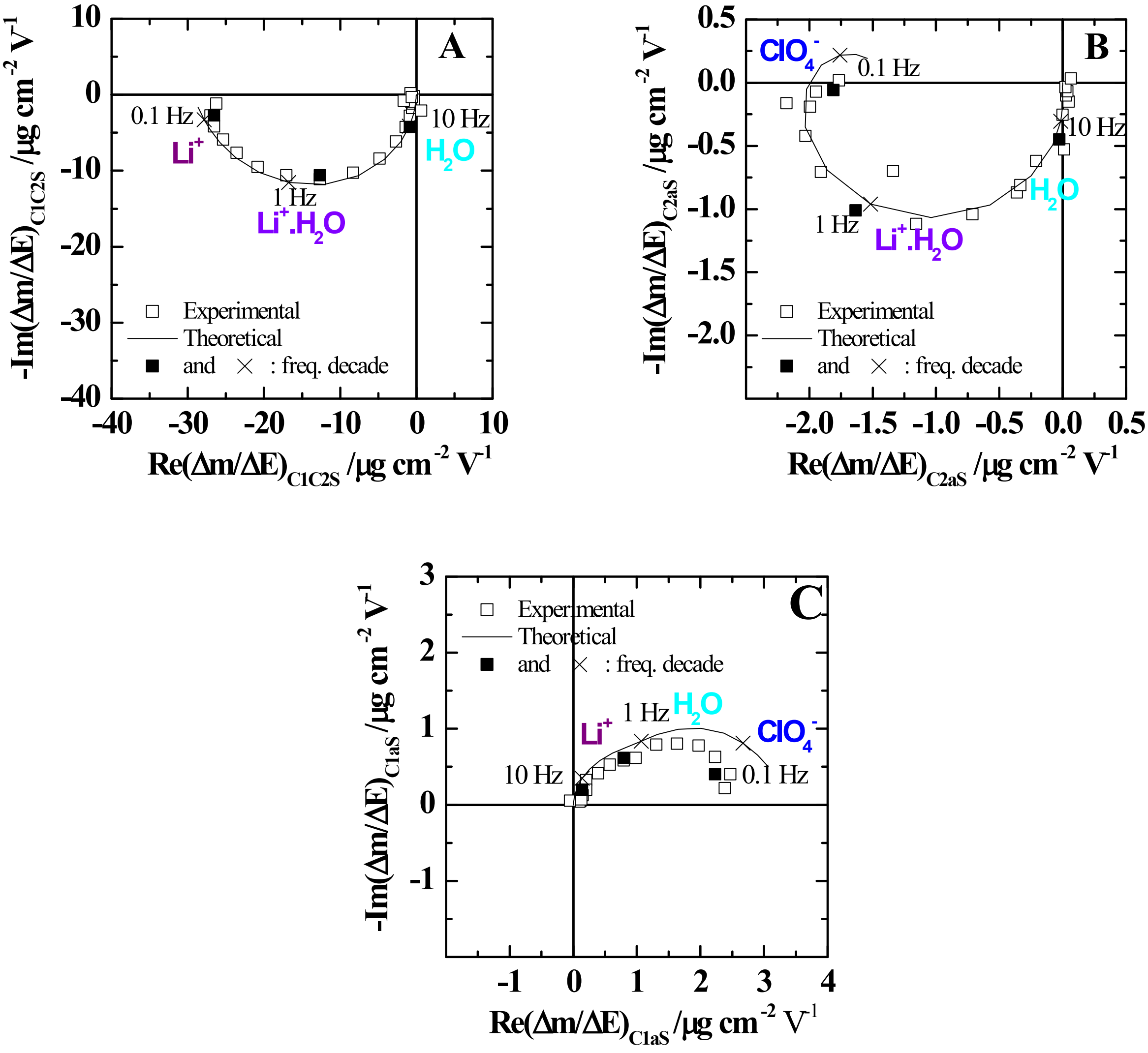

Fig. S5 Three partial transfer functions, for a mesoporous WO_3 thin film, (A) $\left.\frac{\Delta m}{\Delta E}\right|^{c1c2s}(\omega)$, (B) $\left.\frac{\Delta m}{\Delta E}\right|^{c2as}(\omega)$, and (C) $\left.\frac{\Delta m}{\Delta E}\right|^{c1as}(\omega)$, measured in aqueous 0.5 M $LiClO_4$ electrolyte at -0.3 V vs Ag/AgCl (3M KCl saturated with AgCl) (both experimental and theoretical curves are given).