

Enhanced CO₂ sorption in a hybrid PEI - Mo oxide film via pulsed electrodeposition

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S1. Schematic for calculation of PEI adsorption on different Mo-oxide surfaces

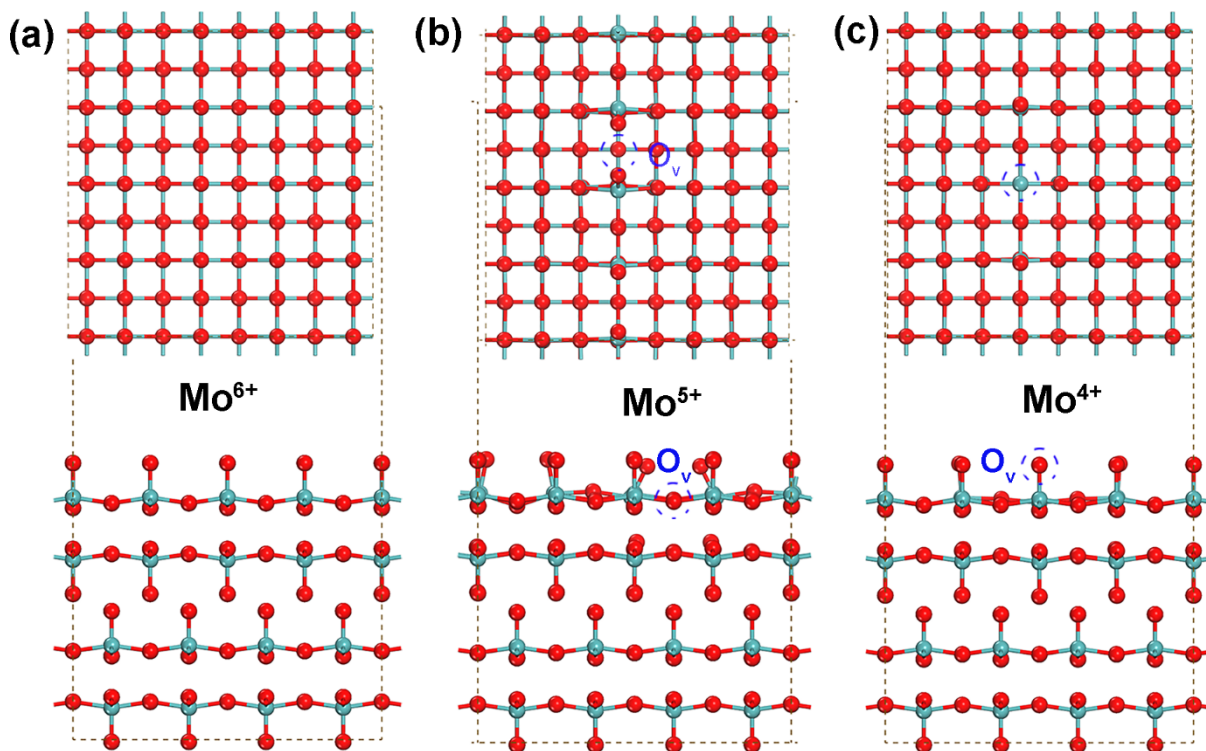
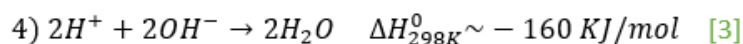
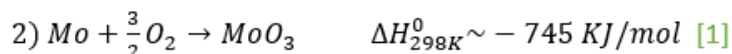
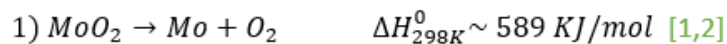
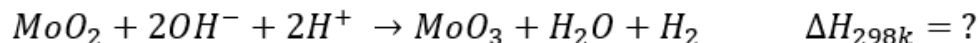


Figure S1. The top and corresponding side view for Mo-oxide surface (a) without defects, representing Mo^{6+} sorption site (b) with oxygen vacancy at the bridge site, representing Mo^{5+} sorption site and (c) with oxygen vacancy at the top site, representing Mo^{4+} sorption site.

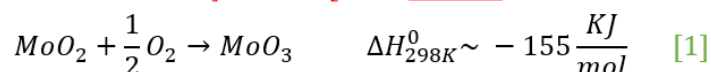
Figure S1 shows the schematic of the model surfaces used for understanding the energetics of Polyethylenimine (PEI) molecule interaction with Mo oxide surfaces. The Mo^{6+} surface (Fig. S1a) uses stoichiometry MoO_3 , while the Mo^{5+} surface (Fig. S1b) is the same surface with an oxygen vacancy at the bridge site, and the Mo^{4+} surface (Fig. S1c) is a surface with oxygen vacancy at the top site.

S2. Calculation for enthalpy of formation for MoO₃



$$\Delta H_{298\text{K}} = -30 < 0$$

Production of MoO₃ from MoO₂ in the literature:



We calculated the enthalpy of formation for conversion of MoO₂ to MoO₃ in the presence of OH⁻ and O₂. Oxidation of MoO₂ to MoO₃, via both OH and O₂ has a negative enthalpy of formation. This means that there is a tendency for the reaction to proceed if the kinetic barrier (eg. availability of reactants) is not high and this is likely the case as the availability of reactants in the electrodeposition process is enhanced by the pulsing method.

References:

[1] Staskiewicz, Bernard A., James R. Tucker, and Paul E. Snyder. "The Heat of Formation of Molybdenum Dioxide and Molybdenum Trioxide1." *Journal of the American Chemical Society* 77.11 (1955): 2987-2989.

[2] Jacob, K. T., et al. "Thermodynamic evidence for phase transition in MoO₂- δ." *The Journal of Chemical Thermodynamics* 39.12 (2007): 1539-1545

[3] Ruscic, Branko, et al. "Introduction to active thermochemical tables: Several "key" enthalpies of formation revisited." *The Journal of Physical Chemistry A* 108.45 (2004): 9979-9997.

S3. XPS depth profile analysis of constant potential deposited PEI Mo-oxide

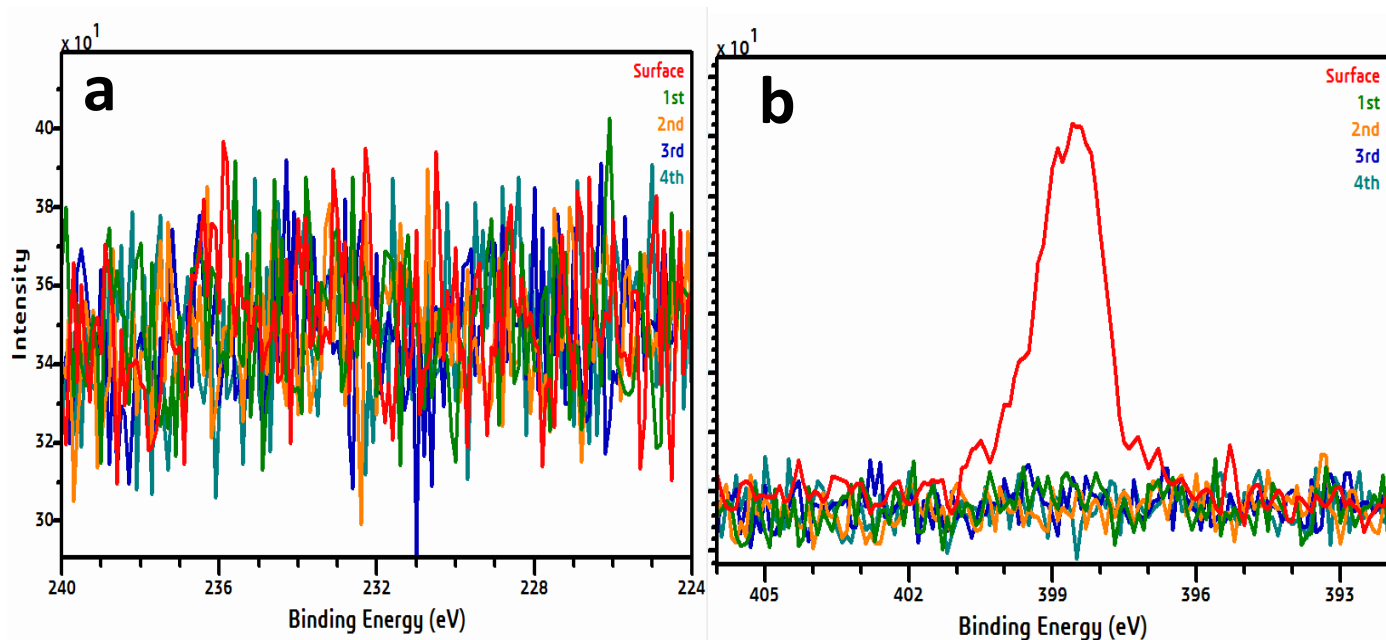


Figure S3. XPS spectra of (a) Mo3d and (b) N1s for constant potential electrodeposited films from Mo-PEI solution. Each of the different scans following the surface scan proceeds after 10 seconds of surface sputtering, thereby representing the chemical depth profiles.

Figure S3 shows the XPS depth profiles of surface/films after electrodeposition with constant potential method using identical Mo-0.25 wt% PEI solution employed for subsequent pulse electrodeposition. It can be observed that we have negligible film deposition from Mo3d scans in Fig. S3a, using the constant potential method that is contrary to deposition at identical conditions in solutions without PEI. The N1s scan in Fig. S3b shows strong signal from PEI, that is removed with light sputtering after 10s. This shows the presence of PEI only on the surface and likely the passivation of the surface. Such passivation can inhibit Mo-oxide film growth.

S4. Investigating PEI interaction on surfaces

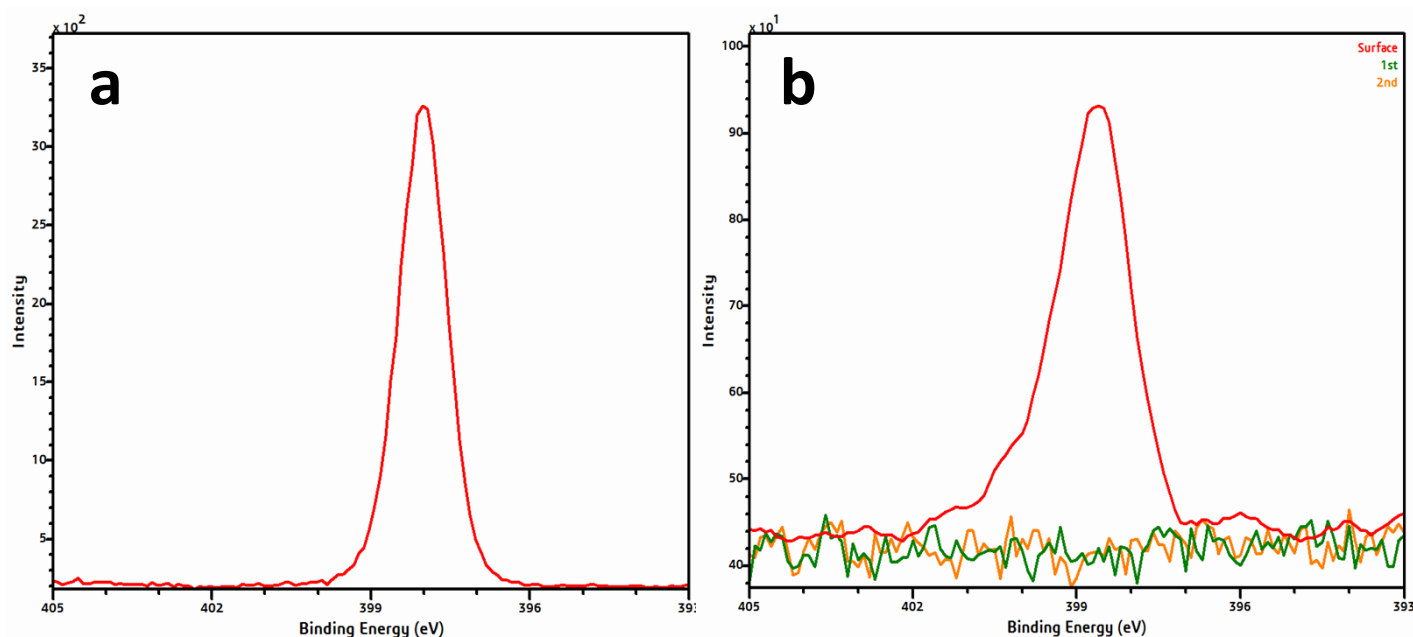


Figure S4. XPS N1s spectra for (a) drop-casted PEI solution on ITO substrate, (b) Immersed ITO in DI water-PEI solution. The 1st and 2nd scans as indicated in Fig. S4b represents depth profile with 10s interval.

Figure S4 shows XPS N1s spectra for drop casted PEI on the ITO substrate (Fig. S4a), together with immersion of the ITO substrate in 0.25wt% PEI solution (Fig. S4b). The films were subsequently rinsed with DI water and dried with nitrogen gun as per other electrodeposition sequences. The results show the similar peak (located at ~ 398.2 eV) on all the surfaces, showing the chemical nature of PEI interaction with the substrate. The depth profile for the immersed substrate also show that this remains a surface effect much like what was observed in S3.

S5. X-ray Diffraction measurements for hybrid and Mo-oxide films

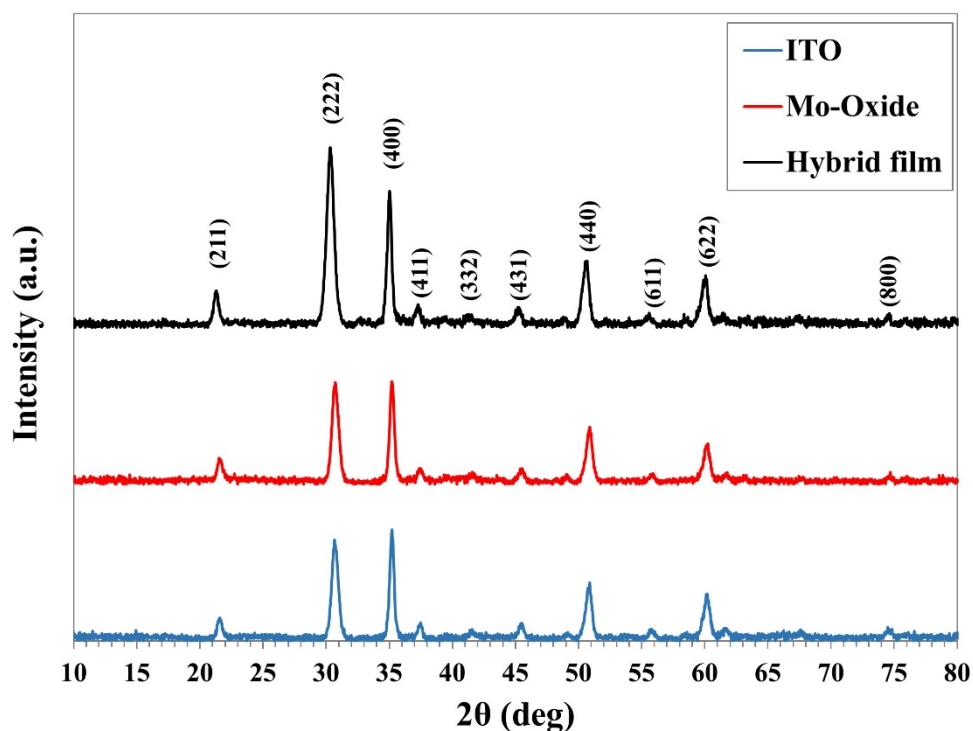


Figure S5. X-ray Diffraction measurements conducted for bare ITO substrate, and respective hybrid (Mo-PEI) and PEI-free electrodeposited film on the identical ITO substrate. The peaks observed can be assigned to respective indicated crystallographic planes of the ITO substrate [1,2].

XRD measurements were conducted by BRUKER D8 ADVANCE diffractometer with step size of 0.02 and in the range of 8 to 85 degrees. Two samples were electrodeposited on ITO using the Pulse B recipe (one from the electrolyte with 0.25wt% PEI and the other without PEI). Fig. S5 shows the diffraction spectrum of the two samples together with a bare ITO substrate for comparison. The results show that all the peaks present can be mapped to that of the ITO substrate and no additional peaks were observed for the thin films. We conclude that the pulsed electrodeposited films, with or without PEI, are amorphous in nature.

[1] Choi, Dongchul, Sung-Jei Hong, and Yongkeun Son. "Characteristics of indium tin oxide (ITO) nanoparticles recovered by lift-off method from TFT-LCD panel scraps." *Materials* 7.12 (2014): 7662-7669.

[2] Thirumoorthi, M., and J. Thomas Joseph Prakash. "Structure, optical and electrical properties of indium tin oxide ultra thin films prepared by jet nebulizer spray pyrolysis technique." *Journal of Asian Ceramic Societies* 4.1 (2016): 124-132.

S6. EDS mapping of the hybrid Mo-PEI film

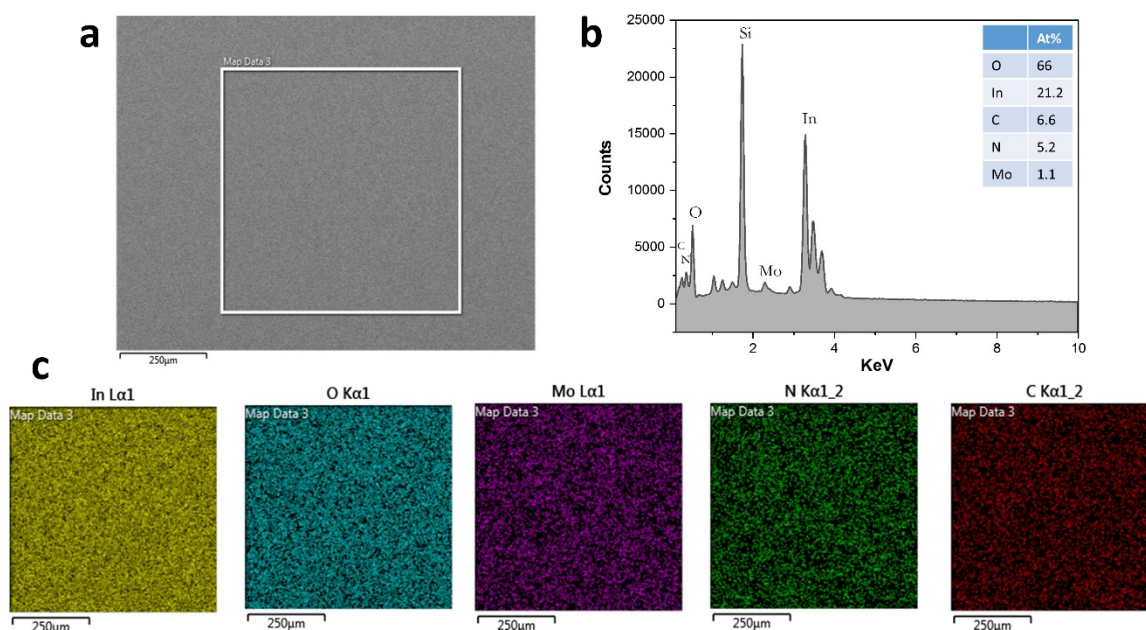


Figure S6. Energy Dispersive X-ray Spectroscopy (EDS) of the Mo-PEI hybrid film. (a) selected area of the surface for the analysis, (b) EDS results based on the atomic percentage of the elements for the film and the substrate, and (c) mapping micrographs of respective elements from the film.

The EDS analysis was carried out in a JEOL 7600F device at an accelerating voltage of 15 kV. The Indium, silicon, and parts of the oxygen signal originates from the substrate which was ITO on the glass. The nitrogen, carbon, and molybdenum are mainly coming from the film structure. In EDS mapping, the interaction volume for the thin film is low and high magnification cannot be easily obtained. The mapping is done at magnification where we can yield reasonable Mo signal. The mapped micrographs show a homogenous distribution of the PEI molecules in the Mo-oxide structure.

S7. Fitted XPS spectrum to obtain PEI/Mo ratio

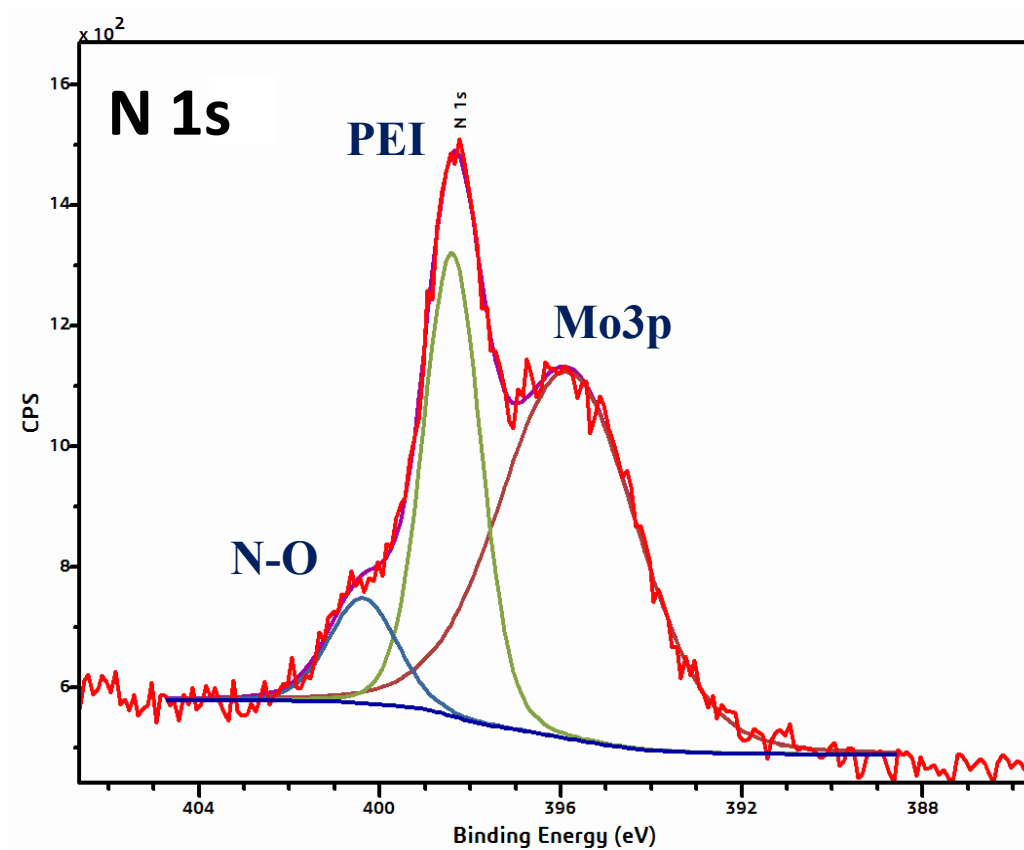


Figure S7. Fitted N1s/Mo3p spectra for pulse electrodeposited Mo-PEI hybrid film.

Fitted XPS spectrum for hybrid film deposited using pulse B recipe. The spectrum is fitted using three different peaks representing Mo3p, PEI and N-O bond. The fitted peaks have binding energies of ~ 395.8 eV, ~ 398.2 eV, and ~ 400.2 eV consistent with those reported in literature [1,2,3].

References:

- [1] Zhou, Weijia, et al. "MoO₂ nanobelts@ nitrogen self-doped MoS₂ nanosheets as effective electrocatalysts for hydrogen evolution reaction." *Journal of Materials Chemistry A* 2.29 (2014): 11358-11364.
- [2] Liu, Xiaobo, et al. "H₂O₂-assisted synthesis of porous N-doped graphene/molybdenum nitride composites with boosted oxygen reduction reaction." *Advanced Materials Interfaces* 4.11 (2017): 1601227.
- [3] Escolástico, Sonia, Simona Somacescu, and José M. Serra. "Tailoring mixed ionic–electronic conduction in H₂ permeable membranes based on the system Nd_{5.5}W_{1-x}Mo_xO_{11.25- δ} ." *Journal of Materials Chemistry A* 3.2 (2015): 719-731.

S8. Cross-section SEM micrograph for Pulse-electrodeposited hybrid PEI Mo-oxide thin film

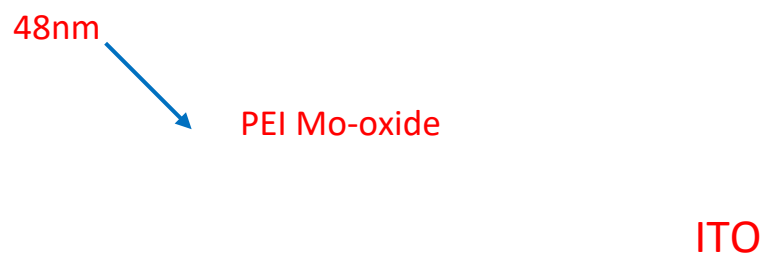


Figure S8. Cross sectional SEM micrograph of pulsed deposited hybrid PEI Mo-oxide thin film on ITO

Cross-section SEM micrographs were obtained by imaging cleaved samples on an FEI Helios 600 at an accelerating voltage of 2 kV and beam current of 21 pA. From Fig. S8, the measured thickness of the Mo-PEI hybrid film is about 48 ± 1 nm. The film was also taken for profilometry analysis which yielded a measurement of 46 ± 1 nm.

S9. Thickness estimation for ultrathin hybrid PEI Mo-oxide films

$$T_{film} = L \cos\theta \ln\left(\frac{R_{exp}}{R_0} + 1\right) \quad L = EAL_{film} = 1.4 (KE = 1254, \beta = 1.2), \cos\theta = 1$$

$$\frac{R_{exp}}{R_0} = \frac{I_{film}^{exp} / I_{sub}^{exp}}{I_{film}^{\infty} / I_{sub}^{\infty}} \quad R_0 = \frac{I_{Mo}^{\infty}}{I_{In}^{\infty}} = \frac{4340.4}{10499.4} = 0.413$$

L = effective attenuation length (EAL)

θ = emission angle of an electron from the surface normal

R_{exp} = intensity ratio of thin film (Mo oxide PEI) to the substrate

R_0 = intensity ratio of pure Mo oxide film to the substrate

Table S8 Recorded signal intensity, ratio and resultant film thickness calculated

PEI loading	R_{exp}	R_{exp}/R_0	T_{film} (nm)
0.5 wt%	0.055	0.133	0.175
1 wt%	0.032	0.077	0.104
3 wt%	0.008	0.019	0.026

For the ultrathin deposited hybrid film, thickness estimation can be accomplished using In3d signal from substrate and Mo3d from the film. This is done using the equation [1] shown above and the estimated thicknesses are shown in the table above. The results show lack of even a full coverage of the hybrid film for the 3 different electrolytes with higher PEI loadings.

References:

- [1] Kim, Kyung Joong, A. Kim, C. S. Kim, S. W. Song, H. Ruh, W. E. S. Unger, J. Radnik et al. "Thickness measurement of nm HfO₂ films." *Metrologia* 58, no. 1A (2021): 08016.
- [2] Powell, Cedric J., and Aleksander Jablonski. "The NIST electron effective-attenuation-length database." *Journal of surface analysis* 9.3 (2002): 322-325.

S10. Comparing CO₂ sorption capacity of other hybrid materials

Material	Synthesis Method	Structure	Sorption capacity (mmol/g)	Test Condition	Reference
Mg- MOF ¹	vapor-assisted crystallization	film	7.7	1 bar	[1]
silica-PEI ² silica-TEPA ³	Impregnation	film	1	800 ppm of CO ₂ and 15% RH	[2]
PEI @ PME ⁴	Hydrothermal/ Impregnation	Powder	7.31	400 ppm CO ₂ 25 °C	[3]
polyethylenimine (PEI) 'snow'	Sol-gel	Powder	10.25	1.02–1.04 bar	[4]
PEI@Ethane-Silica	Hydrothermal/ Impregnation	Nanotube	1	400 ppm CO ₂	[5]
NOHM-I-PEI ⁵ -SIP ⁶	Emulsification	Particles	3.1 1.7	15 vol% CO ₂ 400 ppm CO ₂	[6]

1 = Metal-organic Framework

2 = Polyethylenimine

3 = Tetraethylenepentamine

4 = Extralarge-pore silica (pore-expanded MCM-41)

5 = Nanoparticle organic hybrid materials with ionically tethered polyethylenimine

6 = solvent impregnated polymers

[1] K. J. Kim, J. T. Culp, P. R. Ohodnicki, P. K. Thallapally and J. Tao, *ACS Appl. Mater. Interfaces*, 2021, **13**, 35223–35231.

[2] A. Krishnamurthy, B. Salunkhe, A. Zore, A. Rownaghi, T. Schuman and F. Rezaei, *ACS Appl. Mater. Interfaces*, 2019, **11**, 16594–16604.

[3] A. Sayari, Q. Liu and P. Mishra, *ChemSusChem*, 2016, **9**, 2796–2803.

[4] X. Xu, B. Pejcic, C. Heath, M. B. Myers, C. Doherty, Y. Gozukara and C. D. Wood, *ACS Appl. Mater. Interfaces*, 2019, **11**, 26770–26780.

[5] L. Liu, J. Chen, L. Tao, H. Li and Q. Yang, *ChemNanoMat*, 2020, **6**, 1096–1103.

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S11. Discussion on heat of adsorption for PEI

While the heat of adsorption of CO₂ for the deposited thin film cannot be easily measured, here we attempt to discuss if there will be significant differences in PEI fundamentally based on its heat of adsorption.

Commercially available low-molecular-weight PEI has a carbon/nitrogen ratio of 2:1 and contains a distribution of amine sites, typically 44% primary, 33% secondary, and 22% tertiary amines [1]. The heat of adsorption for the widely used primary amine monoethanolamine (MEA) in aqueous solutions, is around -85 kJ mol⁻¹ while the heat of adsorption for the secondary amine diethanolamine (DEA) is about -72 kJ mol⁻¹. Triethanolamine as a tertiary amine, with the weaker bonds with CO₂ and only in the presence of water, has a heat of adsorption of -48 kJ mol⁻¹ [2].

Interestingly, amines on solid supports appears to yield generally higher negative heat of adsorption. Using DSC measurements, Satyapal et al. obtained a heat of adsorption of -94 kJ mol⁻¹ for branched PEI (BPEI) bonded on a high-surface-area solid poly(methyl methacrylate) [3]. Heat of adsorption for the adsorbent containing 50% and 33% PEI on fumed silica measured to be a -83 and -85 kJ mol⁻¹ by Goeppert et al. [4] However, Knowles et al. using a DTA determined an energy of adsorption for CO₂ on silica grafted with aminosilane of about -50 to -60 kJ mol⁻¹ under dry conditions and -52 to -54 kJ mol⁻¹ under humid conditions [5]. Our recent work using DFT reports an adsorption energy of CO₂ on Mo⁴⁺ defect to be ~-77 kJ/mol [6].

Therefore, overall, we do not expect the heat of sorption of PEI to be fundamentally different and hence do not expect a drastic improvement in sorption efficacy purely based on PEI fundamental properties.

References:

[1] Potter, Matthew E., Simon H. Pang, and Christopher W. Jones. "Adsorption microcalorimetry of CO₂ in confined aminopolymers." *Langmuir* 33.1 (2017): 117-124.

[2] Zhang, Hang, et al. "Applicability of linear polyethylenimine supported on nano-silica for the adsorption of CO₂ from various sources including dry air." *RSC Advances* 5.65 (2015): 52550-52562.

[3] Satyapal, Sunita, et al. "Performance and properties of a solid amine sorbent for carbon dioxide removal in space life support applications." *Energy & Fuels* 15.2 (2001): 250-255.

[4] Goeppert, Alain, et al. "Easily regenerable solid adsorbents based on polyamines for carbon dioxide capture from the air." *ChemSusChem* 7.5 (2014): 1386-1397.

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[6] Tanhaei Mohammad, et al. "Direct control of defects in molybdenum oxide and understanding their high CO₂ sorption performance." *Journal of Materials Chemistry A* 8.25 (2020): 12576-12585.