# Potential Dependent Degradation of Spinel $LiMn_2O_4$ (LMO) and Related Structures Assessed via Manganese-, and Oxygen-Sensitive Scanning Electrochemical Microscopy

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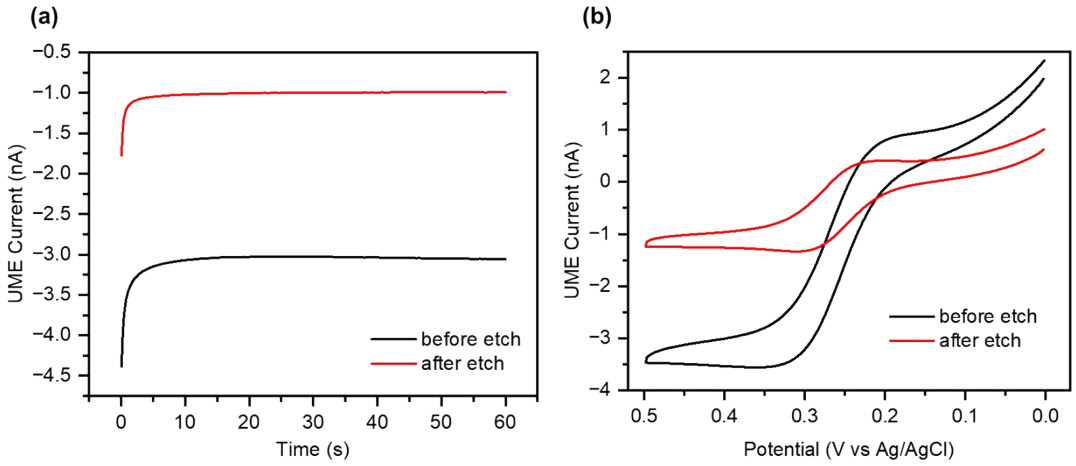


**Figure S1.** Electrochemical characterization of etched Pt UME. (a) Chronoamperometry at 0.1 V (vs Ag/AgCl) and (b) CV of the Pt UME before and after the etching process.

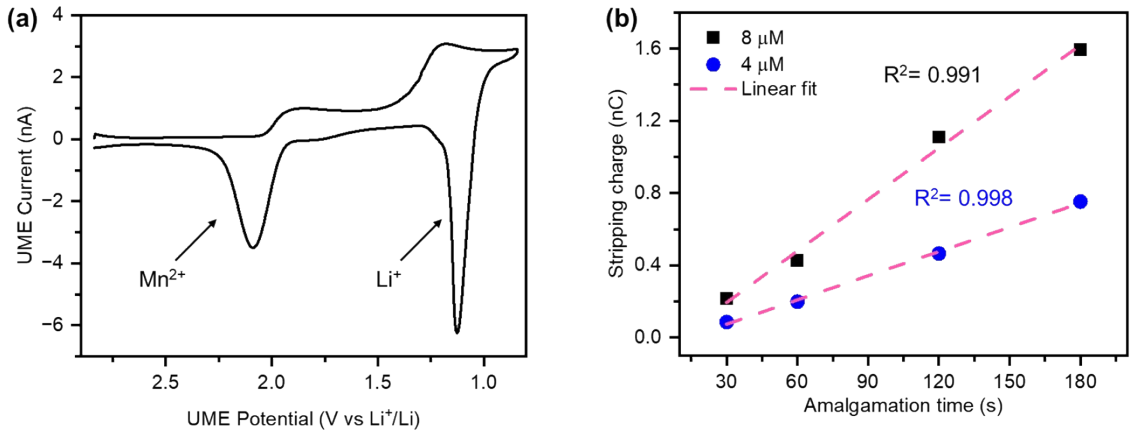


**Figure S2.** Characterization of Hg UME. (a) CV at Hg UME in the solution with $Mn(TFSI)_2$ and $LiPF_6$. (b) Stripping charges of 4μM and 8μM $Mn(TFSI)_2$ solutions with different amalgamation time.

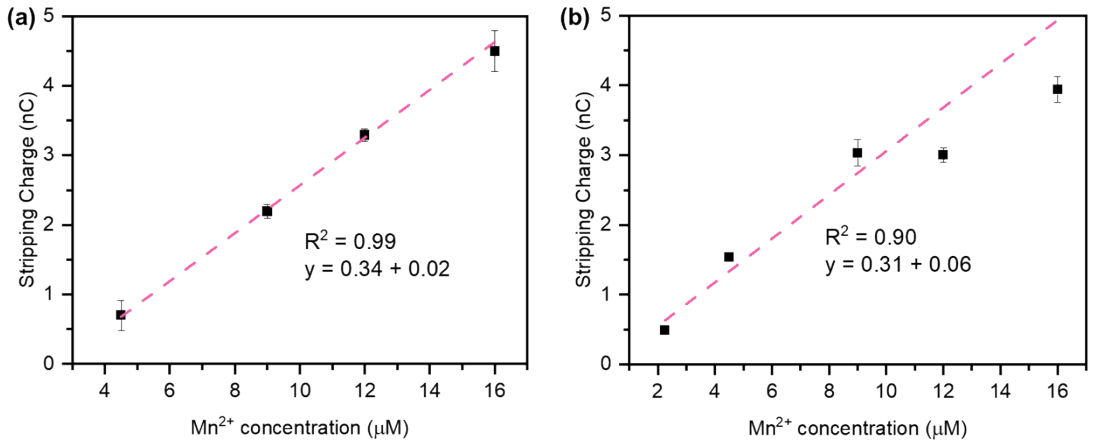


**Figure S3.** Calibration curves of Hg UMEs fabricated on different days. The etching depth and the Hg deposition time were constant for all experiments. The slope of three calibration curves (including the one in **Figure 1c**) is 0.31± 0.02 nC/μM.

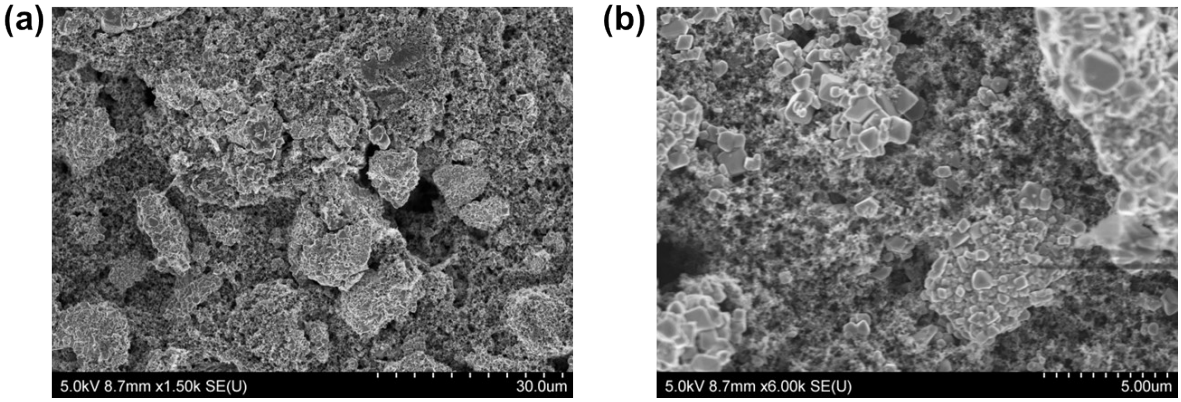


**Figure S4.** SEM images of commercial LMO electrode (pristine) used as a substrate for SECM experiments.

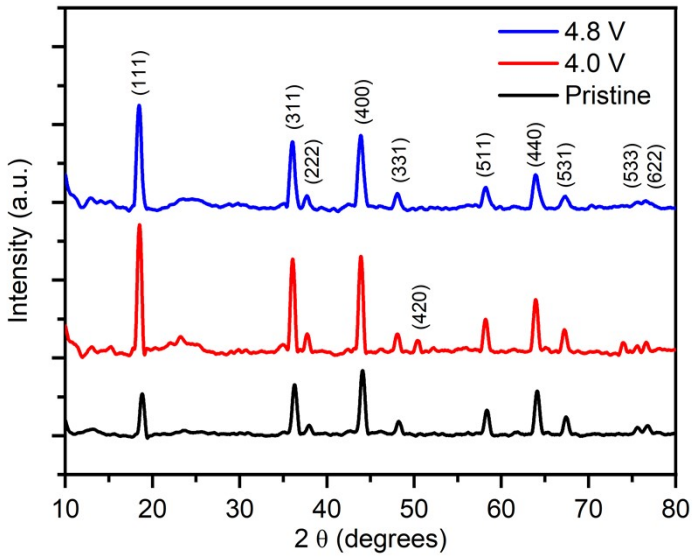


**Figure S5.** XRD spectrum of commercial LMO electrode used as a substrate for SECM experiments. Each curve corresponds to the samples collected at a different state of charge.

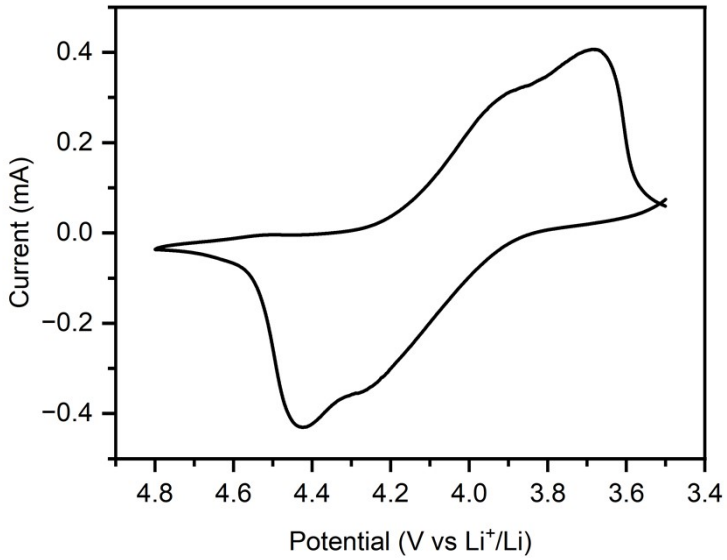


**Figure S6.** CV of commercial LMO electrode used as a substrate for SECM experiments.

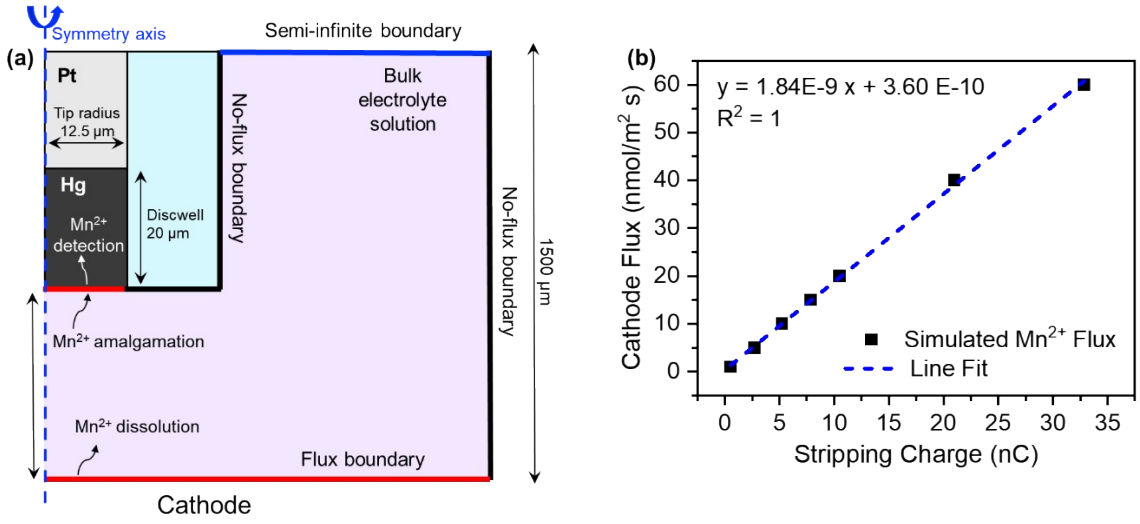


**Figure S7.** Details on COMSOL model used to obtain the $Mn^{2+}$ flux values. (a) 2D geometry used in the COMSOL model and (b) calibration curve that correlates Hg UME stripping charge from the ASV measurements and the corresponding $Mn^{2+}$ flux from the cathode.

**Table S1.** Variables and parameters used in the COMSOL model.

| Variable | Value [unit] | Description |
|---|---|---|
| a | 12.5 [um] | radius of UME |
| alpha | 0.5 | Butler-volmer transfer coefficient |
| D_elec | 3e-10 [m2/s] | Diffusion coefficient of $Mn^{2+}$ in electrolyte |
| D_Hg | 1e-9 [m2/s] | Diffusion coefficient of $Mn^{2+}$ in Hg phase |
| distance | 15 [um] | |
| E0_ume | 2.1 [V] | E0 of $Mn^{2+}$ amalgamation |
| k0_ume | 0.0005 [cm/s] | standard rate constant for amalgamation |
| RG | 6 | Normalized glass radius |
| T | 298 [K] | temperature |
| eta_ume | Eapp_ume-E0ume | UME overpotential |
| kf_ume | k0_ume*exp((-alpha*F_const*eta_ume)/(R_const*T)) | forward reaction constant |
| kb_ume | k0_ume*exp(((1-alpha)*F_const*eta_ume)/(R_const*T)) | backward reaction constant |

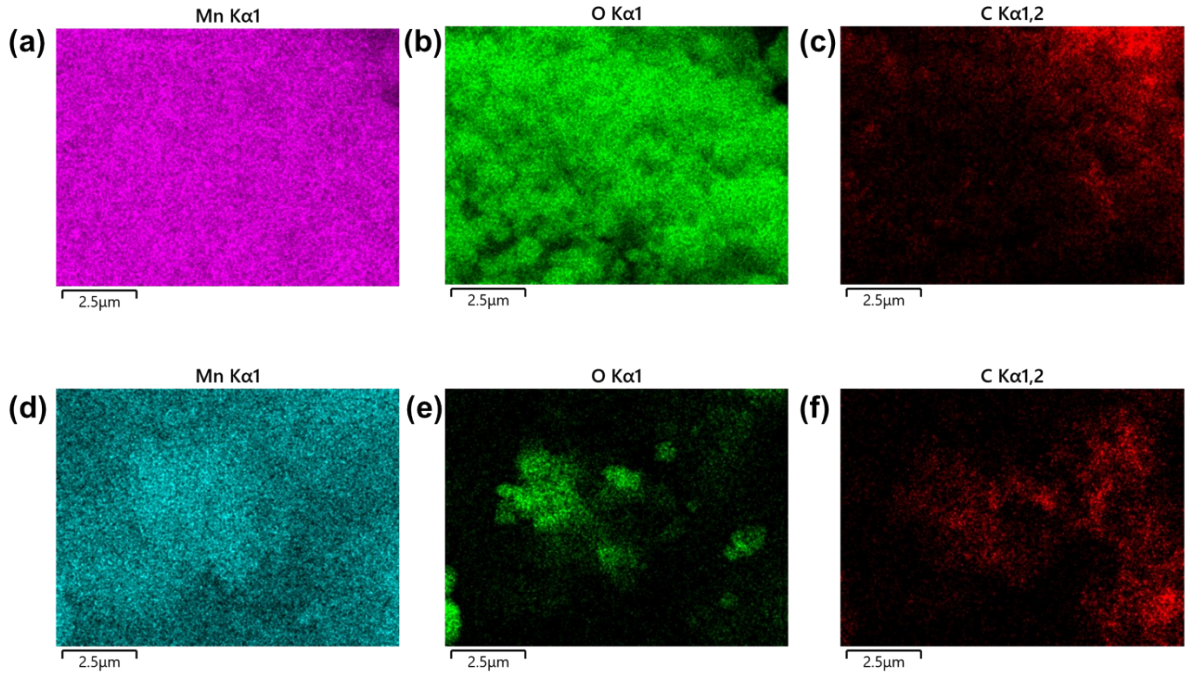


**Figure S8.** EDX elemental mapping of commercial LMO electrode (pristine) on two different sites: site 1 (a-c) and site 2 (d-f).

**Table S2.** EDX elemental data table of commercial LMO electrode (pristine) on two different sites. Site 1 corresponds to the EDX mapping of Figure S8 a-c and site 2 corresponds to the EDX mapping of Figure S8 d-f.

| | **Element** | **O** | **C** | **Mn** | **Al** |
|---|---|---|---|---|---|
| **Site 1** | **At %** | 56.5 | 22.8 | 19.4 | 1.3 |
| **Site 2** | **At %** | 16.6 | 45.9 | 36.8 | 0.6 |

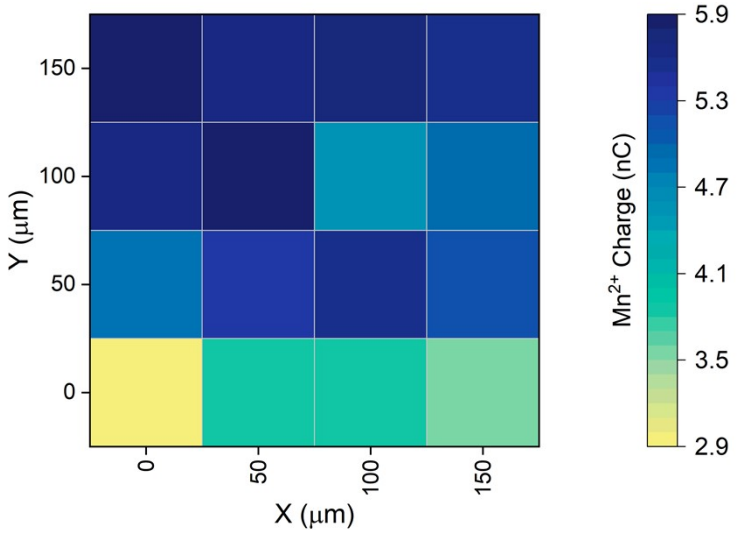


**Figure S9.** SECM mapping of Mn-dissolution from different sites of LMO using Hg UME. The average $Mn^{2+}$ charge was 4.9 ± 0.9 nC. For SECM mapping, LMO was held at 4.5 V for 30 minutes prior to any Mn measurement. Then, ASV measurement at Hg UME with a 1-minute amalgamation time was performed at each location.

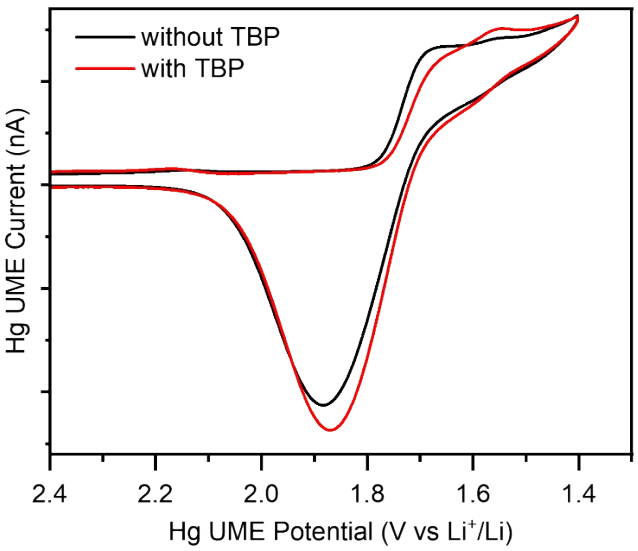


**Figure S10.** CV of $Mn^{2+}$ ion at Hg UME with and without TBP additive

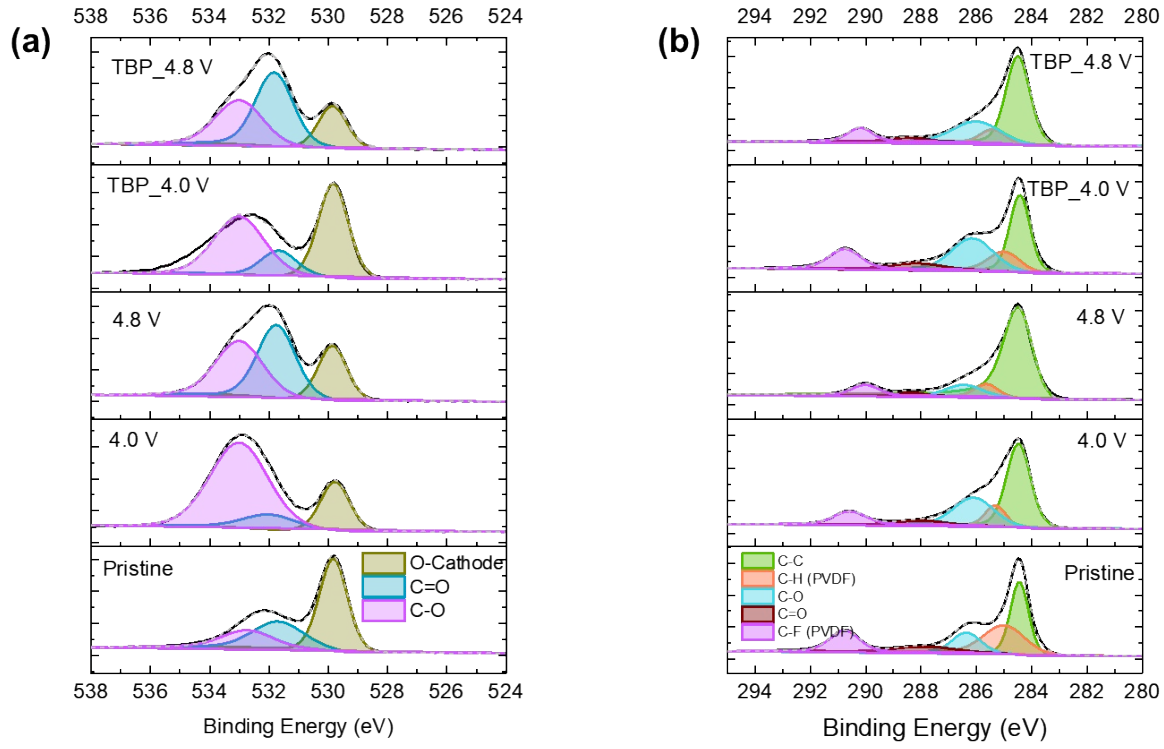


**Figure S11.** XPS (a) O1s and (b) C1s spectra of LMO samples collected at different state-of-charge with and without TBP in the electrolyte.

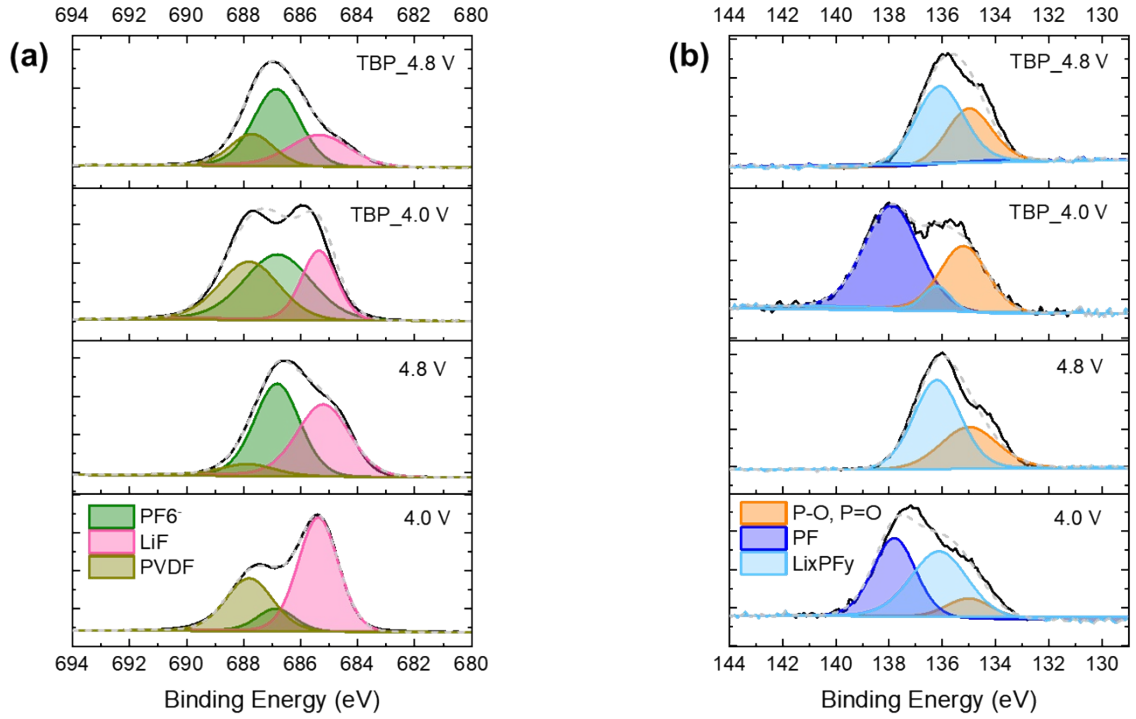


**Figure S12.** XPS (a) F1s and (b) P2p spectra of LMO samples collected at different state-of-charge with and without TBP in the electrolyte.

**Table S3**. Peak assignment for different components in XPS spectra

| Spectra | Assignment | Peak Position (eV) |
|---|---|---|
| O1s | O-Cathode | 529.8 |
| | C=O | 532 |
| | C-O | 532.8 |
| C1s | C-C (conductive C) | 284.4 |
| | C-H (PVDF) | 285 |
| | C-O | 286.3 |
| | C=O | 287.9 |
| | C-F(PVDF) | 290.8 |
| F1s | LiF | 685.4 |
| | PVDF | 687.8 |
| | $LiPF_6$ | 686.8 |
| P2p | P-O, P=O | 135 |
| | $LiPF_6$ (P-F) | 137.8 |
| | LixPFy | 136.1 |

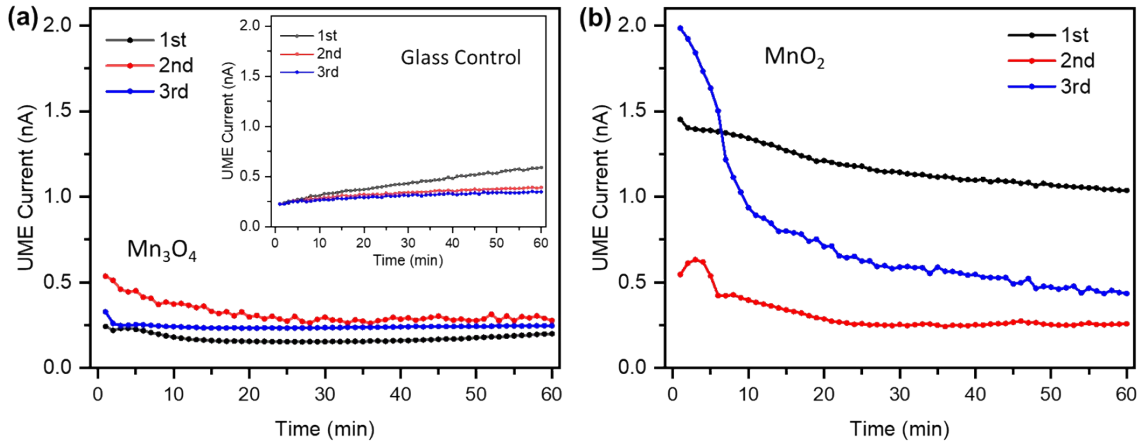


**Figure S13.** Oxygen measurement on (a) $Mn_3O_4$ and (b) **λ**-$MnO_2$ substrates via SECM. The substrates were held at 4.2 V for 1 hour. The inset in (a) depicts the SECM experiment on glass as a control measurement.

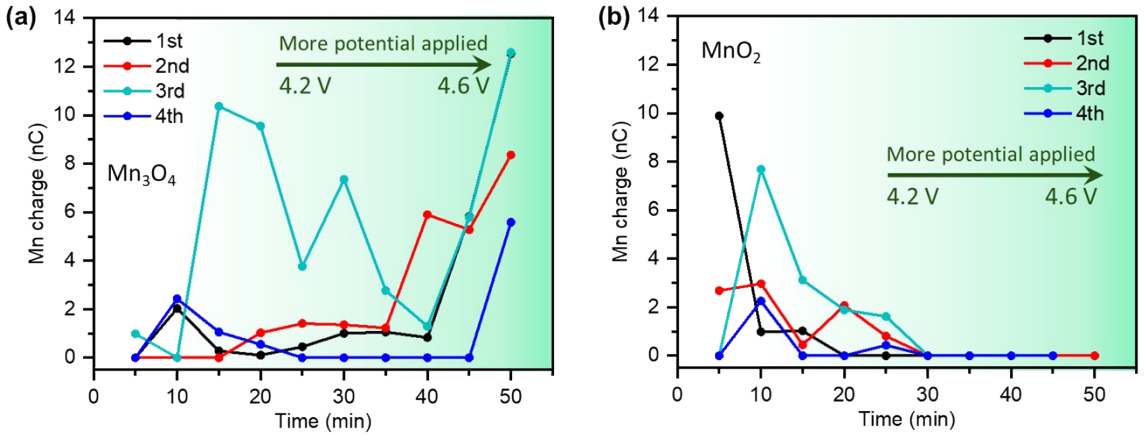


**Figure S14.** Mn measurement on (a) $Mn_3O_4$ and (b) λ-$MnO_2$ via SECM. The substrates were held at OCP initially, then increased to 4.2 V, 4.4 V and 4.6 V.

**Table S4.** Parameters in SECM experiment on $Mn_3O_4$ and λ-$MnO_2$

| $Mn_3O_4$ | OCP | 4.2 V | 4.4 V | 4.6 V |
|---|---|---|---|---|
| 1st | 20 min | 20 min | 5 min | 5 min |
| 2nd | 15 min | 20 min | 10 min | 5 min |
| 3rd | 25 min | 15 min | 5 min | 5 min |
| 4th | 20 min | 20 min | 5 min | 5 min |
| λ-$MnO_2$ | OCP | 4.2 V | 4.4 V | 4.6 V |
| 1st | 20 min | 5 min | 5 min | 5 min |
| 2nd | 20 min | 20 min | 5 min | 5 min |
| 3rd | 20 min | 20 min | N/A | N/A |
| 4th | 20 min | 20 min | 5 min | N/A |