Supplementary Information

Micro-area investigation on electrochemical performance improvement with Co and Mn doping in PbO_2 electrode materials

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Theoretical calculation of RG

$$RG = \frac{rg}{a} \quad [1]$$

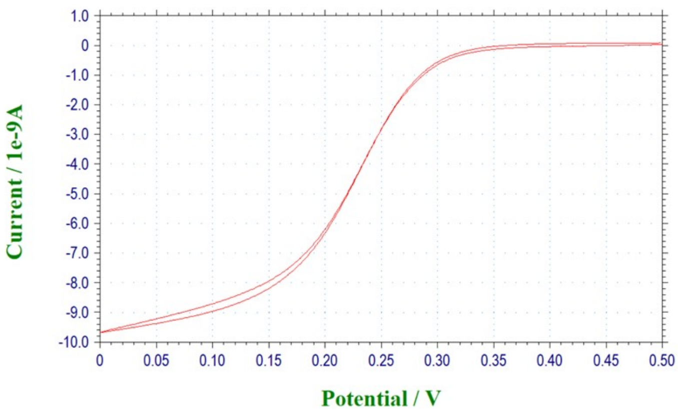
$$L = \frac{d}{a} \quad [2]$$

$$Ni_T(L,RG) = \frac{\frac{2.08}{RG^{0.358}}\left(L - \frac{0.145}{RG}\right) + 1.585}{\frac{2.08}{RG^{0.358}}(L + 0.0023RG) + 1.57 + \frac{\mathrm{In}RG}{L} + \frac{2}{\pi RG}\mathrm{In}\Big(1 + \cdots}$$
[3]

Where rg is the radius of the insulating sheath; a is the radius of the conductive radius. The value of RG was attained from a negative approach curve operating on a piece of quartz glass.[1]

Before using the probe in each experiment, the probe must be electropolished. Electrochemically polished by cyclic voltammetry from −0.5 V to 2.0 V in a 0.5 mol·L^{-1} H_2SO_4 solution, and 35 cycles at least are required, the sweep rate is 5 mV·s^{-1}.

CV of the probe in the steady state during the experiment



Theoretical calculation of hemispherical diffusion

$$I_{tip,\infty} = 4nFDaC^0 \quad [4]$$

where n is the number of transferred electrons, F is the Faraday constant, D is the diffusion coefficient, a is the tip radius, and C^0 the bulk concentration of the reactant.[2,3]

Theoretical calculation of SECM tip approach curves

$$Ni_T(L,RG,\kappa) = Ni_T^{cond}\left(L+\frac{1}{\kappa},RG\right) + \frac{Ni_T^{ins}(L,RG)}{(1+2.47RG^{0.31}L\kappa)(1+L^{0.006RG}\cdots}$$

[5]

$$Ni_T^{ins}(L,RG) = \frac{\frac{2.08}{RG^{0.358}}\left(L-\frac{0.145}{RG}\right)+1.585}{\frac{2.08}{RG^{0.358}}(L+0.0023RG)+1.57+\frac{\text{In}RG}{L}+\frac{2}{\pi R\cdots}}$$

[6]

$$Ni_T^{cond}\left(L+\frac{1}{\kappa},RG\right) = \alpha(RG)+\frac{1}{\beta(RG)}\frac{\pi}{4ArcTan\,L}+\left(1-\alpha(RG)-\frac{1}{2\beta(R\cdots}\right.$$

$\text{Tan}\,L$ [7]

$$\alpha(RG) = \ln 2+\ln 2\left(1-\frac{2}{\pi}ArcCos\frac{1}{RG}\right)-\ln 2\left[1-\left(\frac{2}{\pi}ArcCos\frac{1}{R\cdots}\right.\right.$$

$$\beta(RG) = 1+0.639\left(1-\frac{2}{\pi}ArcCos\frac{1}{RG}\right)-0.186\left[1-\left(\frac{2}{\pi}ArcCos\frac{\cdots}{R\cdots}\right.\right.$$

Where Ni_T, Ni_T^{ins} and Ni_T^{cond} represent the normalized current for a kinetically controlled substrate、an insulating substrate (i.e., no mediator generation) and a diffusion-controlled conducting substrate (i.e. fast regeneration of a redox mediator), respectively.[2,3]

FIGURES

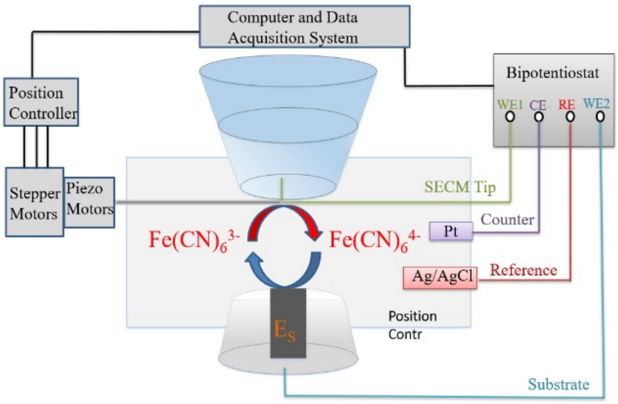


Figure S1. SECM Instruments

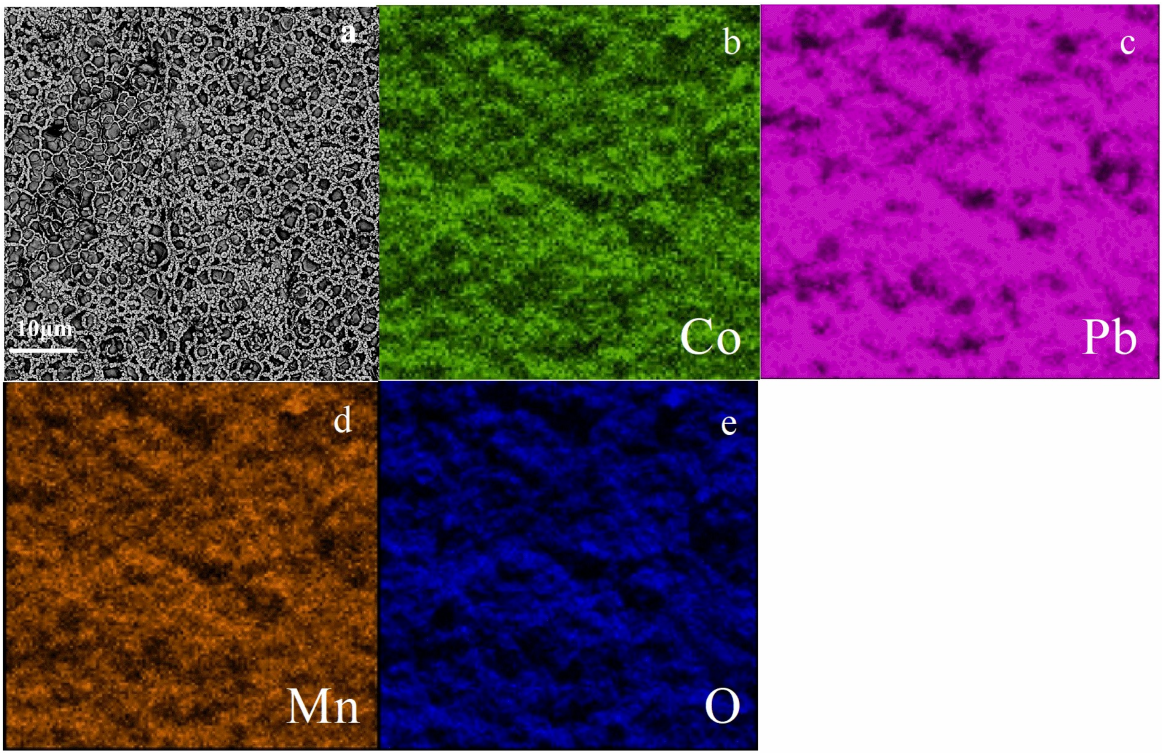


Figure S2 SEM image along with the corresponding EDX elemental maps for individual Co, Pb, Mn and O elements of PbO_2-Co_3O_4-MnO_2.

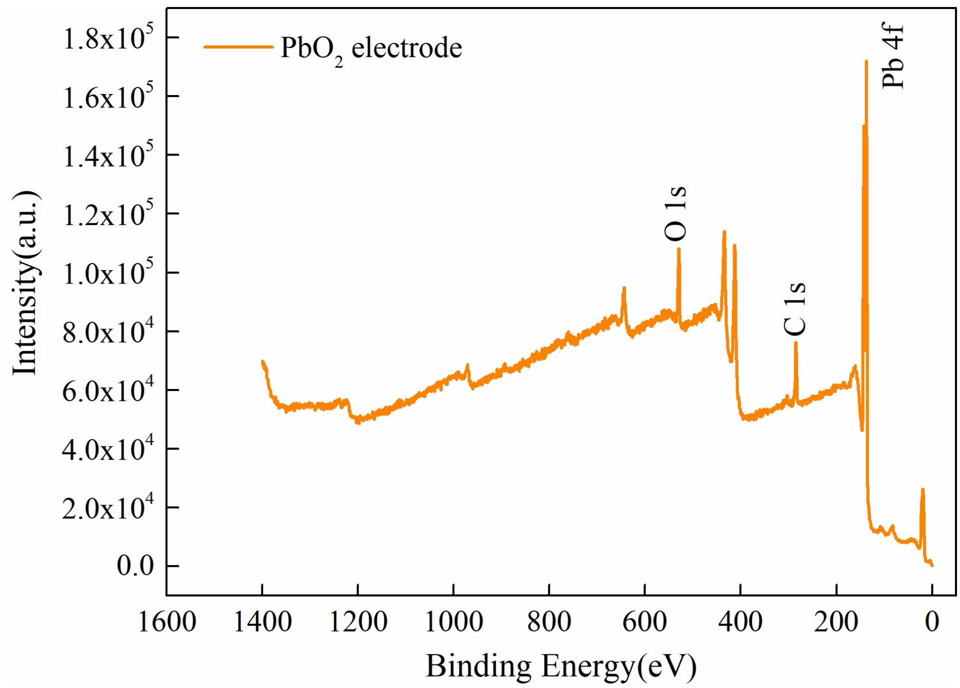


Figure S3. XPS spectra of PbO_2 electrode.

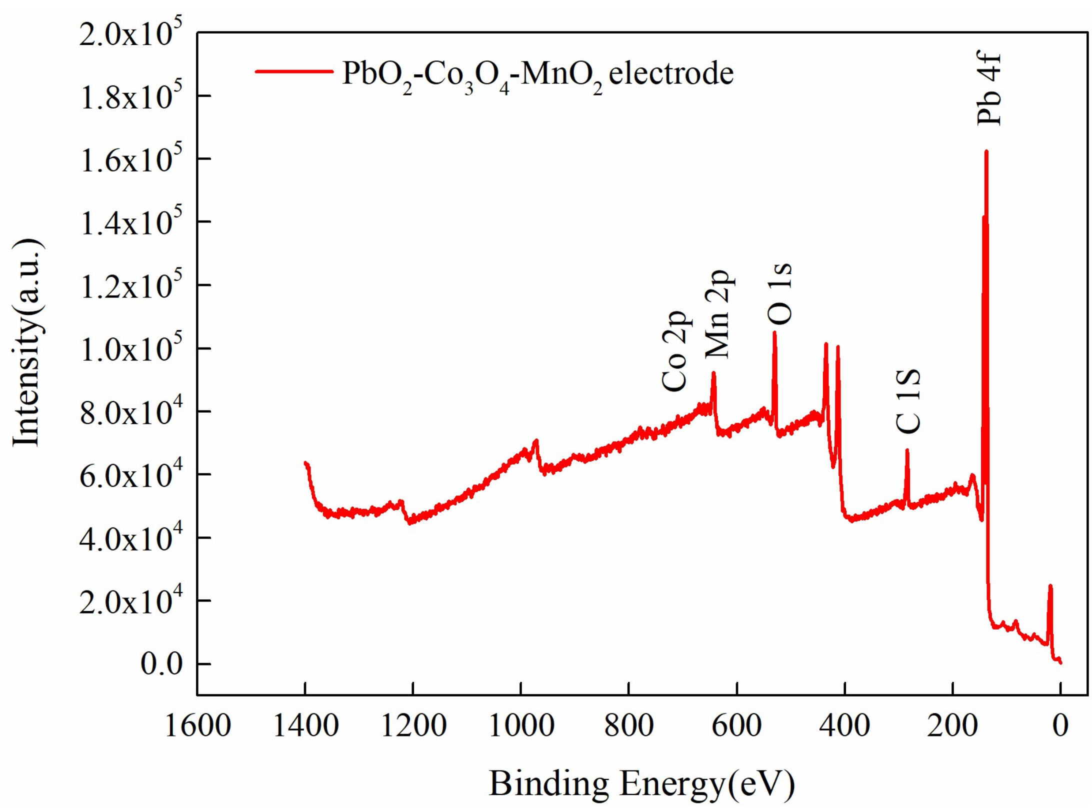


Figure S4. XPS spectra of PbO_2-Co_3O_4-MnO_2 electrode.

References

[1] R. Cornut, S. Griveau, C. Lefrou, Accuracy study on fitting procedure of kinetics SECM feedback experiments, J. Electroanal. Chem. 2010; 650: 55-7.

[2] Bard AJ, Fan FRF, Kwak J, Lev O. Scanning electrochemical microscopy. Introduction and principles. Analytical Chemistry. 1989; 61: 132-8.

[3] Wei C, Bard AJ, Mirkin MV. Scanning Electrochemical Microscopy. 31. Application of SECM to the Study of Charge Transfer Processes at the Liquid/Liquid Interface. The Journal of Physical Chemistry. 1995; 99: 16033-42.