Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Synthesis of Mesoporous $LiMn_2O_4$ and $LiMn_{2-x}Co_xO_4$ Thin Films Using MASA Approach as Efficient Water Oxidation Electrocatalysts.

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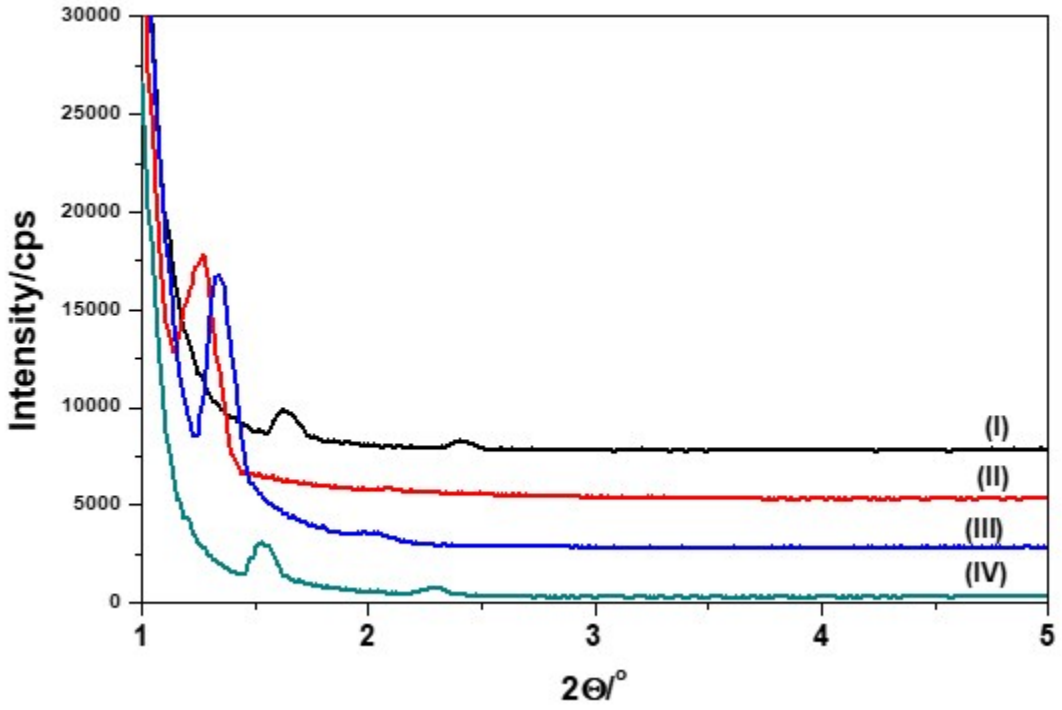

Figure S1. Small angle XRD patterns of fresh samples of 60 salt/P123 and various CTAB/P123 ratios, (I) 0, (II) 1, (III) 3, and (IV) 5.

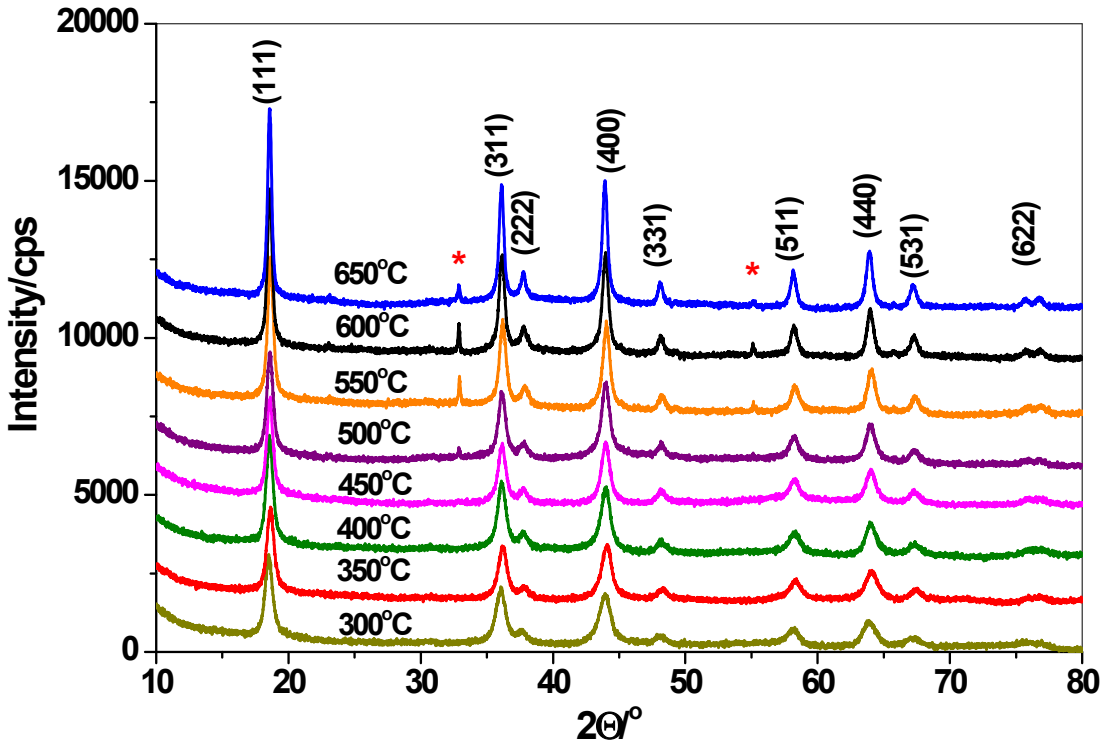

Figure S2. XRD patterns of meso-$LiMn_2O_4$, calcined at 300-650 °C, bottom to top (indexed using PDF card of JCPDS 044-0145).

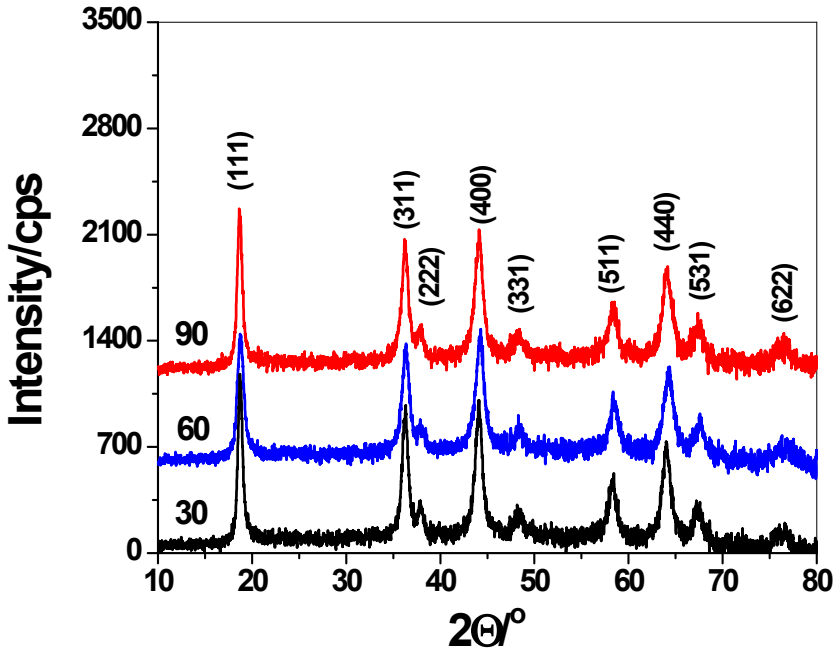

Figure S3. XRD pattern of meso-$LiMn_2O_4$, prepared using 30, 60, and 90 salt/P123 mole ratios, bottom to top, respectively.

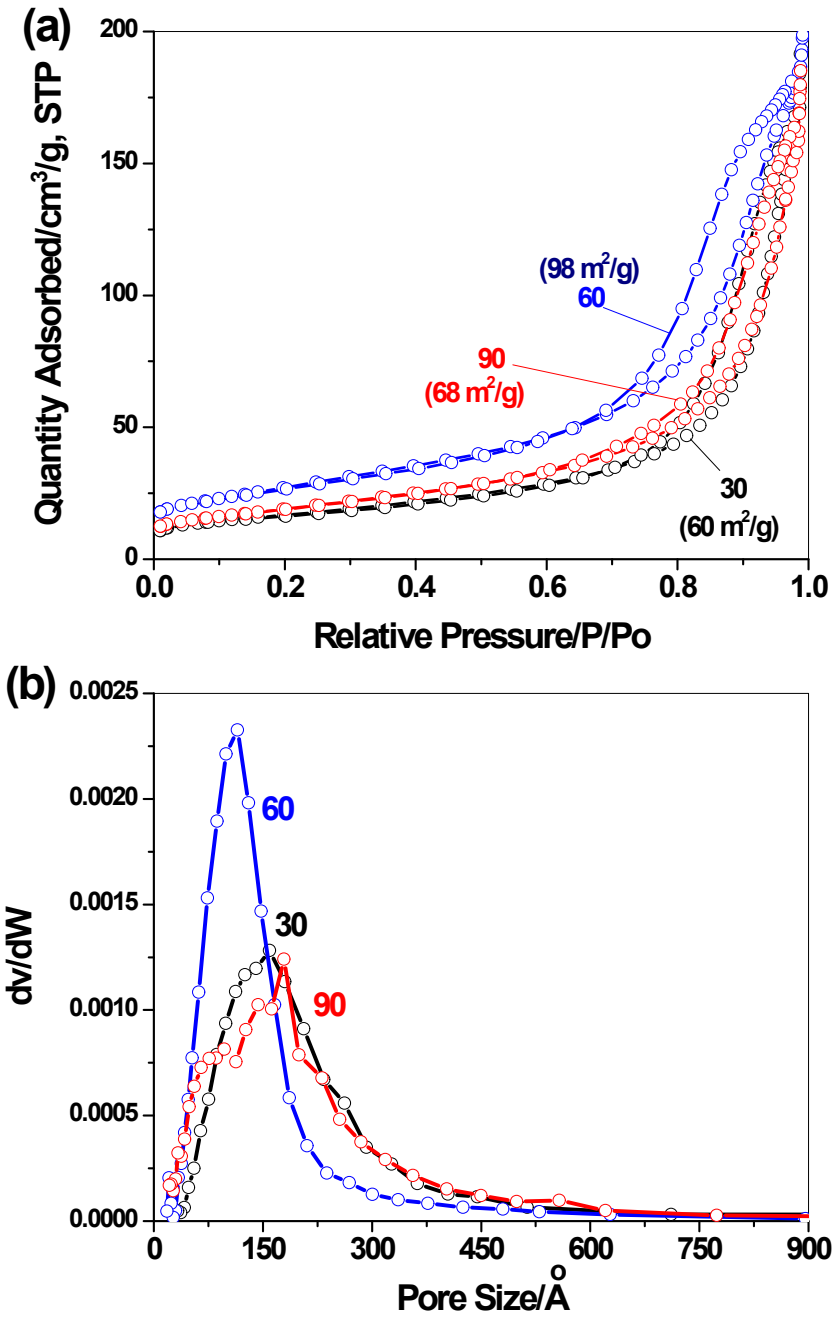

Figure S4. N_2(77.4K) sorption isotherms (a) and BJH pore size distribution plots (b) of meso-$LiMn_2O_4$, prepared using 30, 60, and 90 salt/P123 mole ratios.

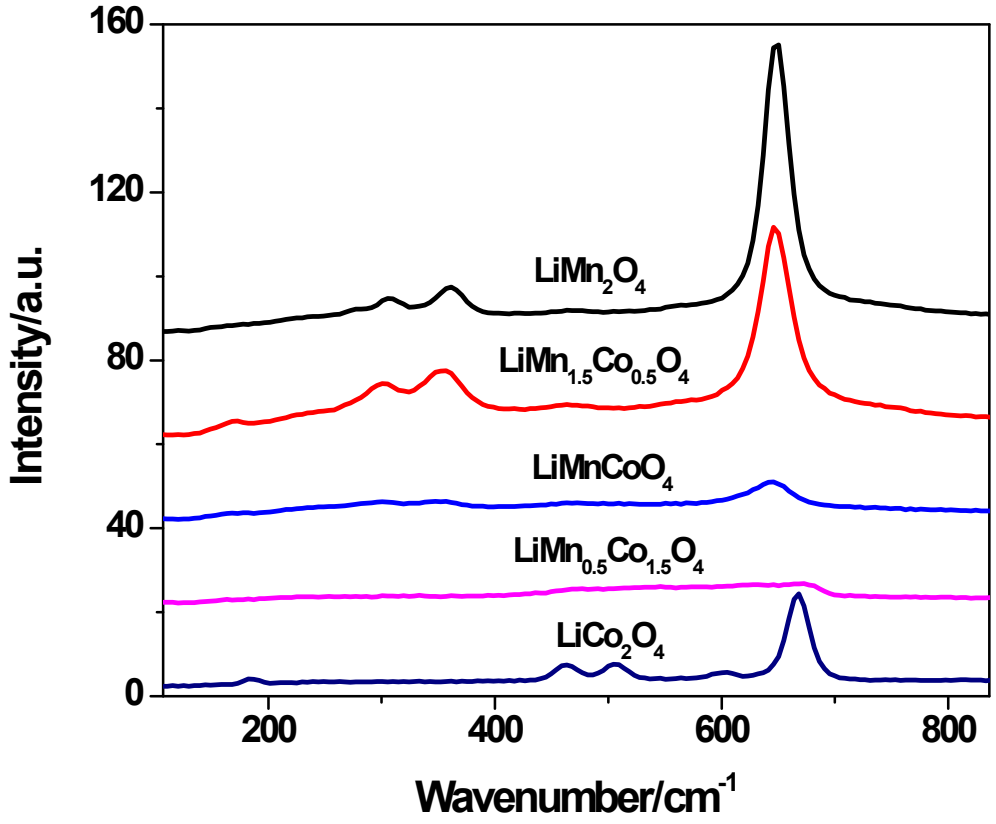

Figure S5. Raman spectra of meso-$LiMn_{1-x}Co_xO_4$.

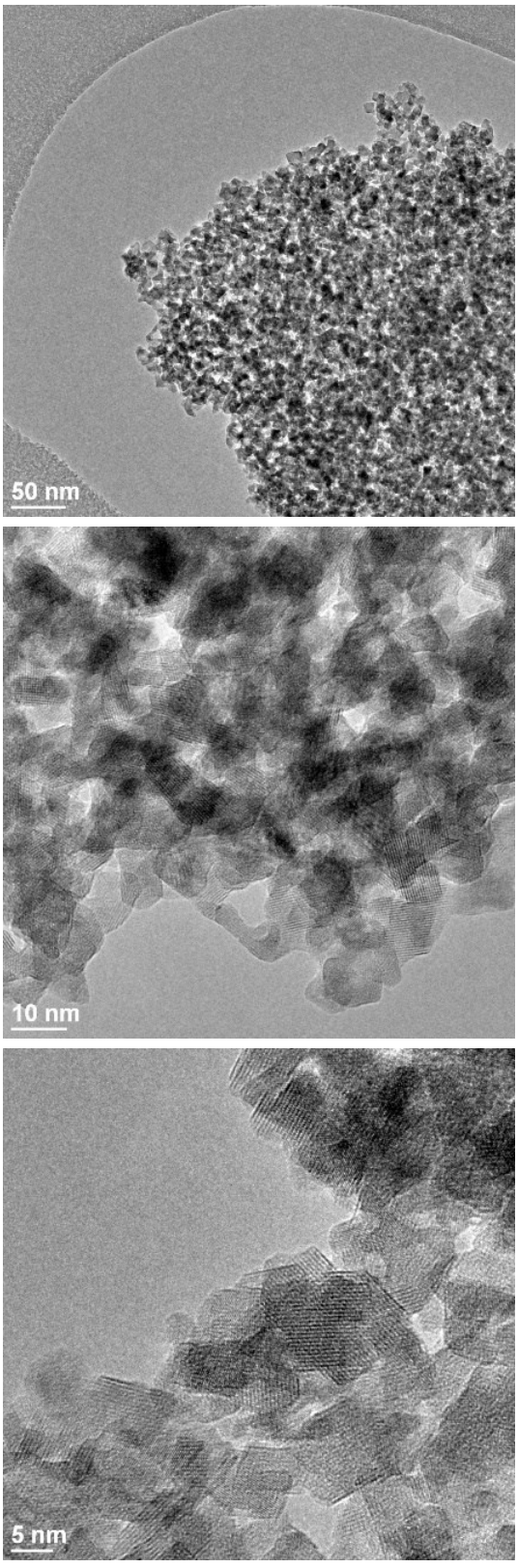

Figure S6. TEM images of meso-$LiMnCoO_4$ at various magnifications.

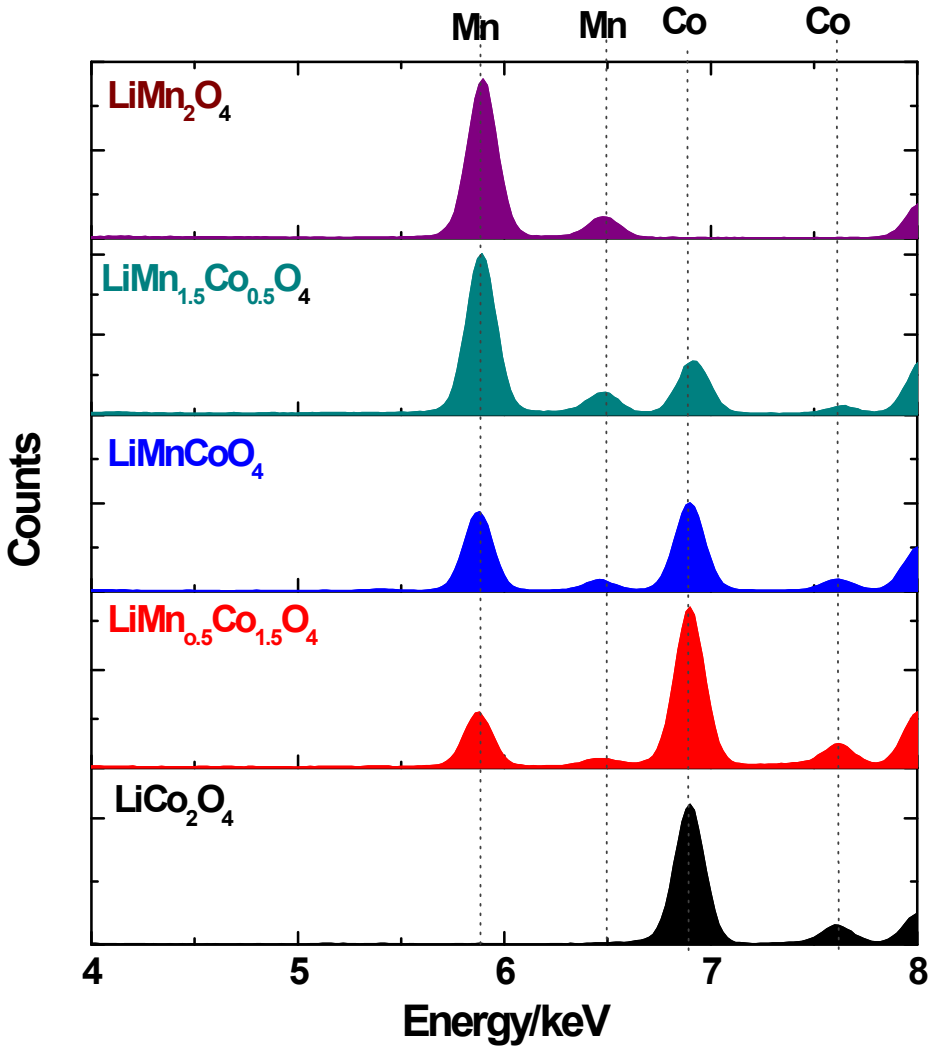

Figure S7. EDX spectra of meso-$LiMn_{2-x}Co_xO_4$.

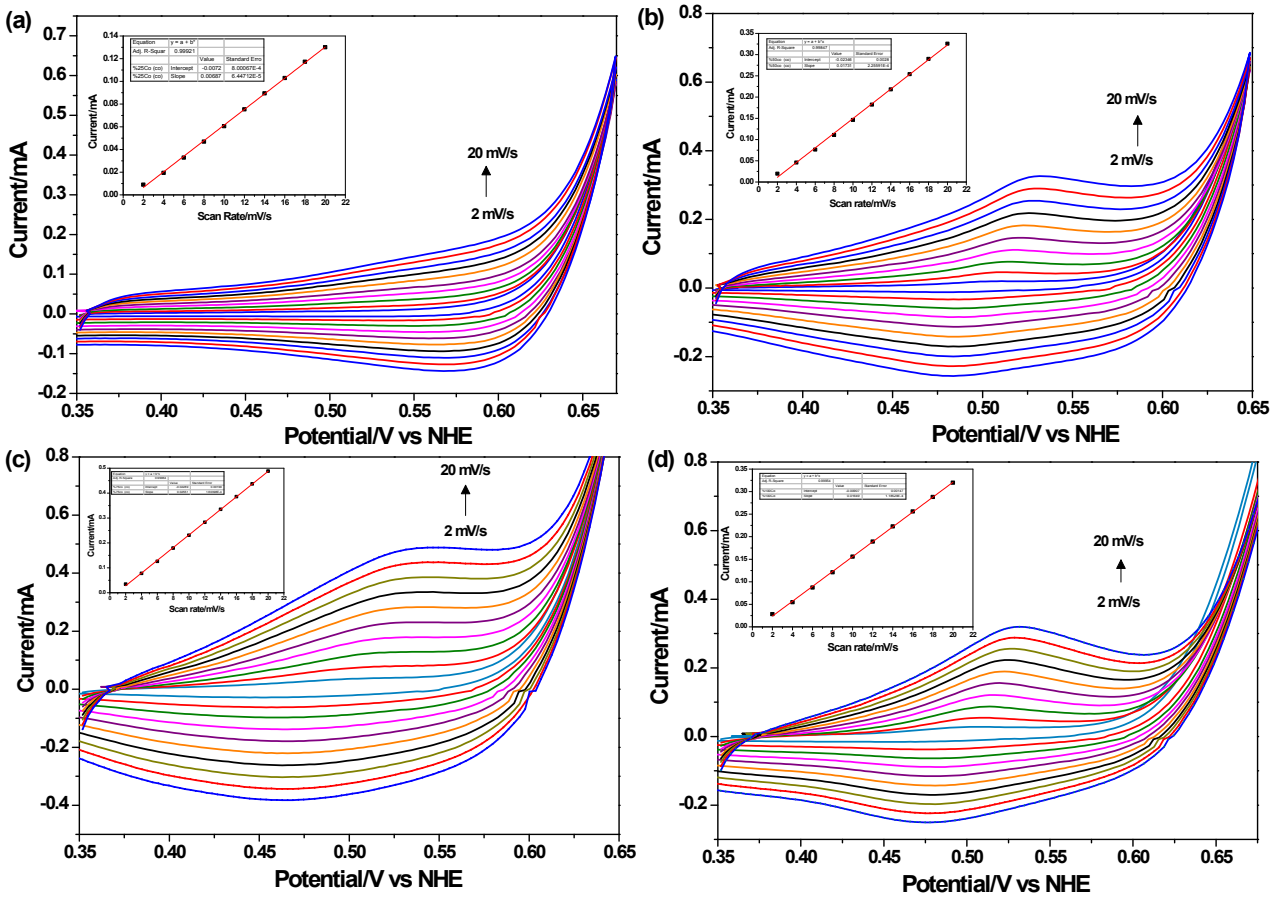

Figure S8. CVs of $LiMn_{2-x}Co_xO_4$ with different scan rate (2-20 mV/s), x is (a) 1.5, (b) 1.0, (c) 0.5 and (d) 0.0. Inset shows linearity of current density of $Co^{2+/3+}$ oxidation peak versus scan rate.

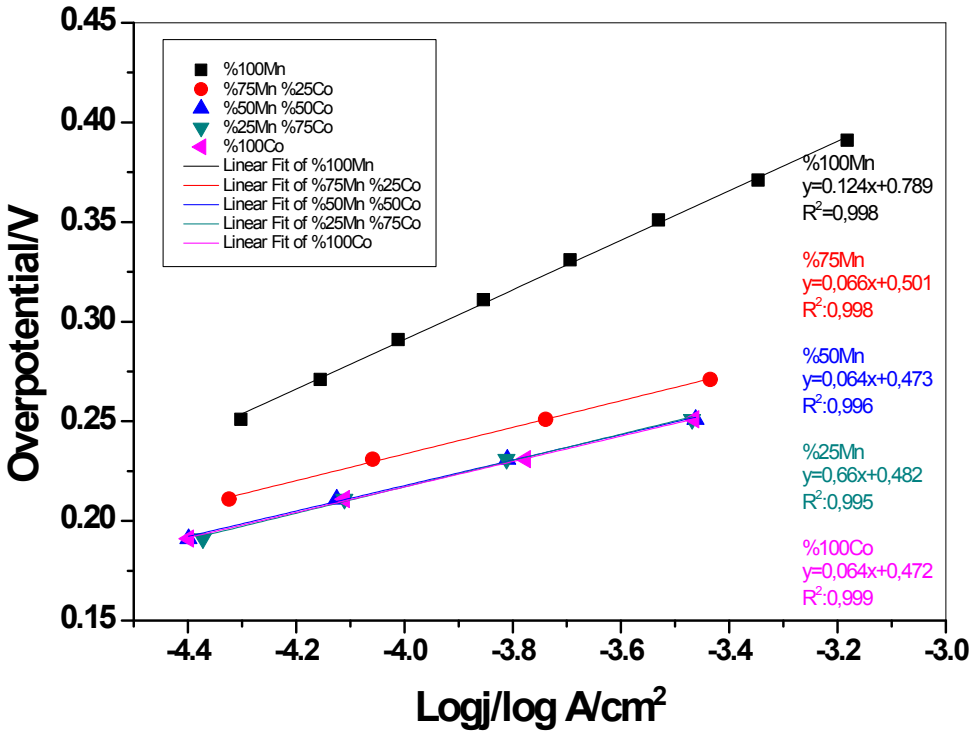

Figure S9. Tafel plots obtained for $LiMn_{2-x}Co_xO_4$ modified electrodes at pH 13.6.

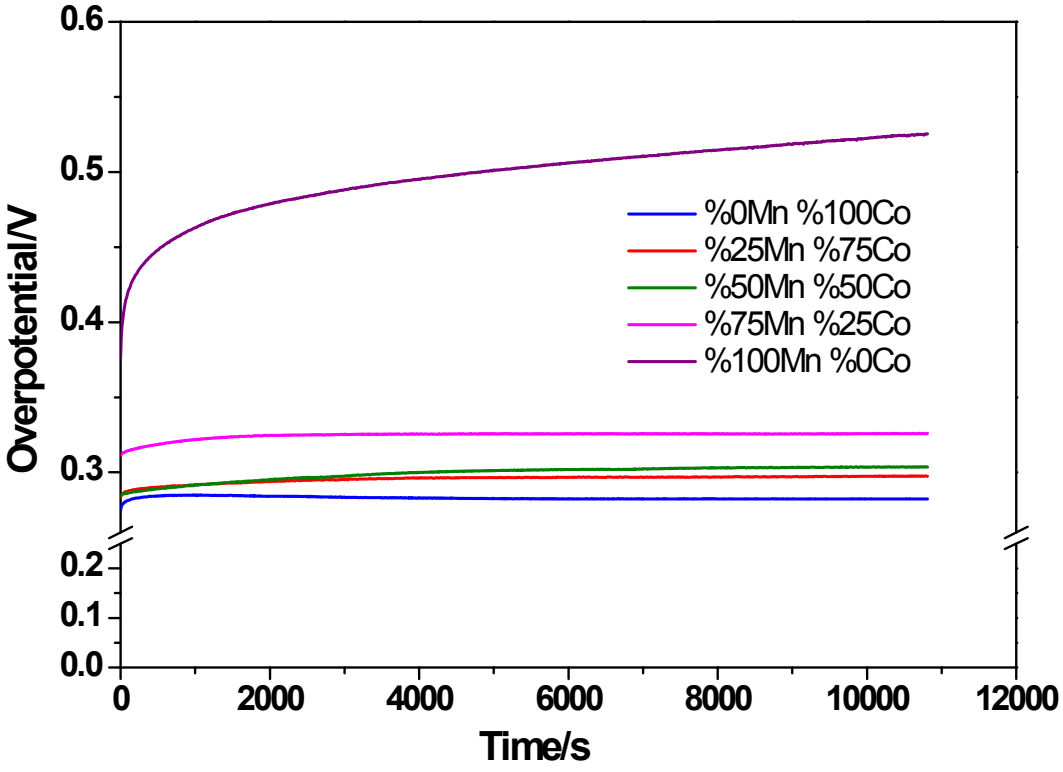

Figure S10. Chronopotentiometric experiments performed on electrodes at pH 13.6 at a current density of 1 mA cm^{-2} for three hours.

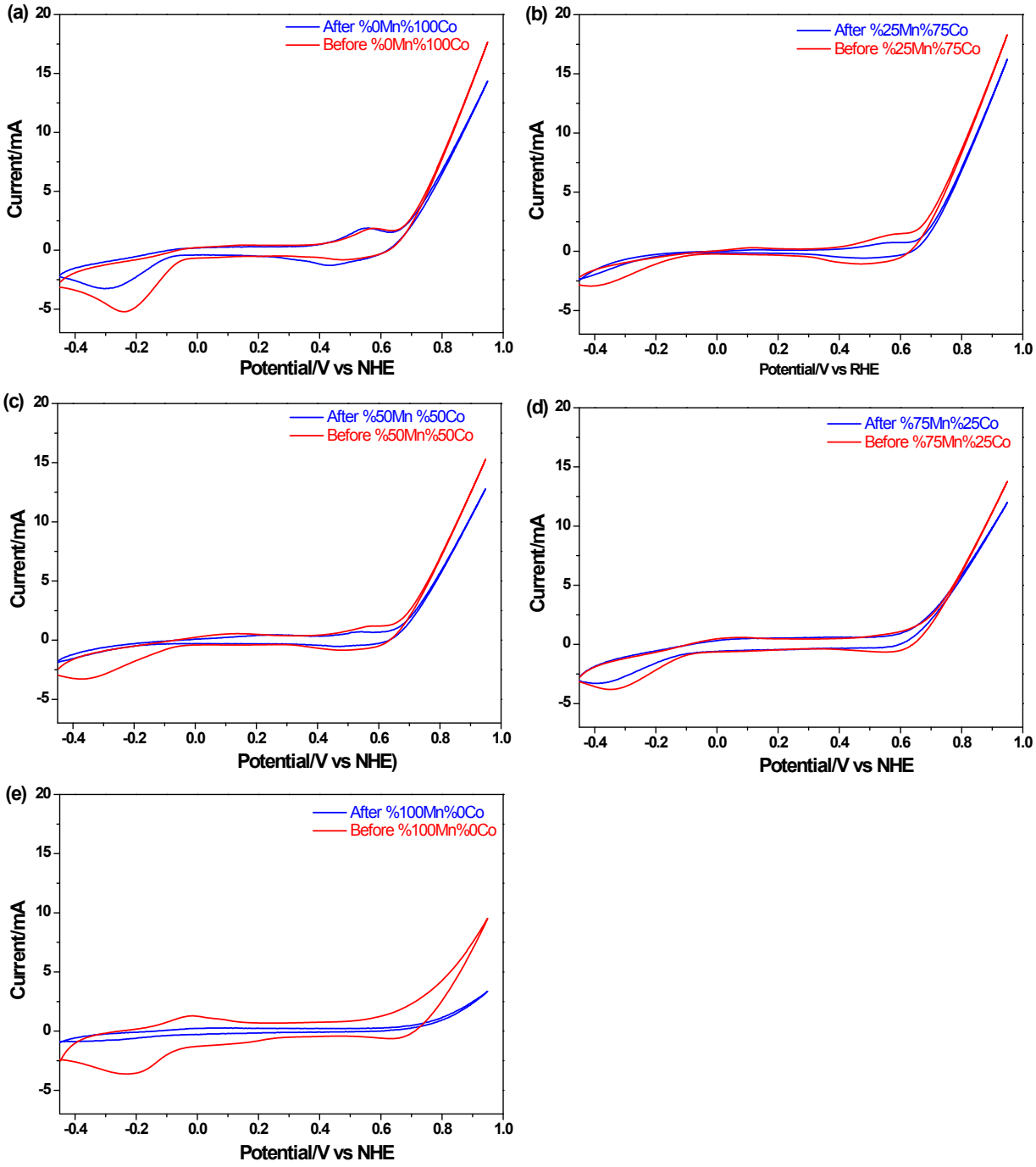

Figure S11. CVs performed on electrodes before (red curves) and after (blue curves) chronopotentiometric experiment displayed in Figure S8.

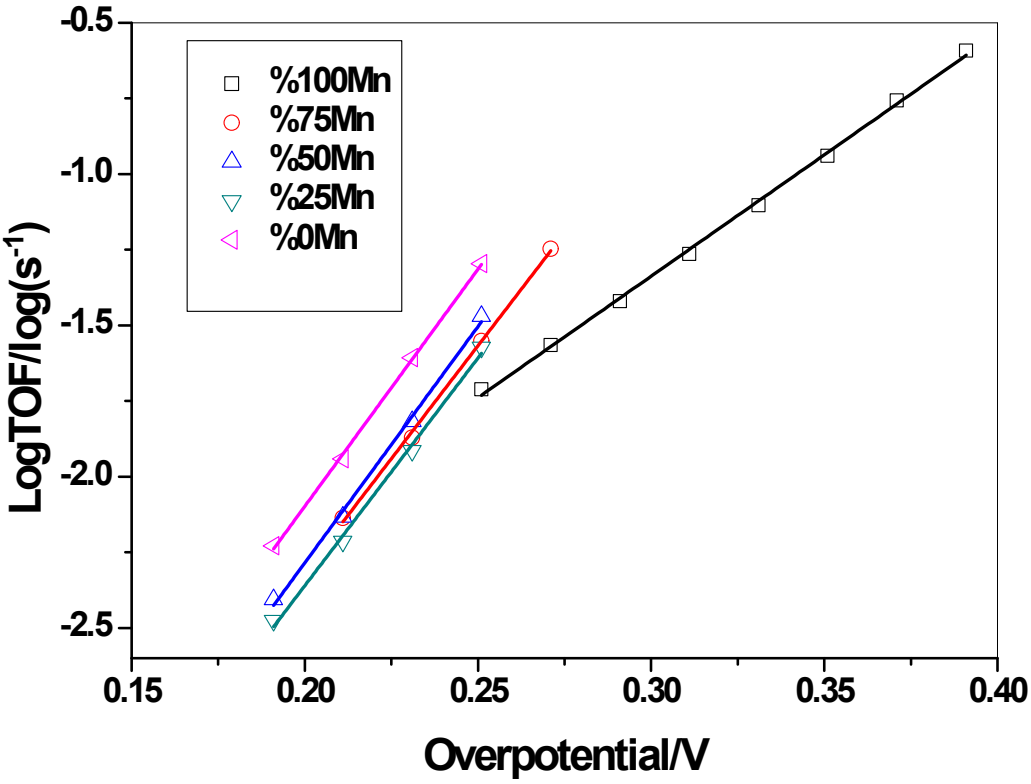

Figure S12. Dependence of turnover frequencies of $LiMn_{2-x}Co_xO_4$ modified electrodes recorded at pH = 13.6

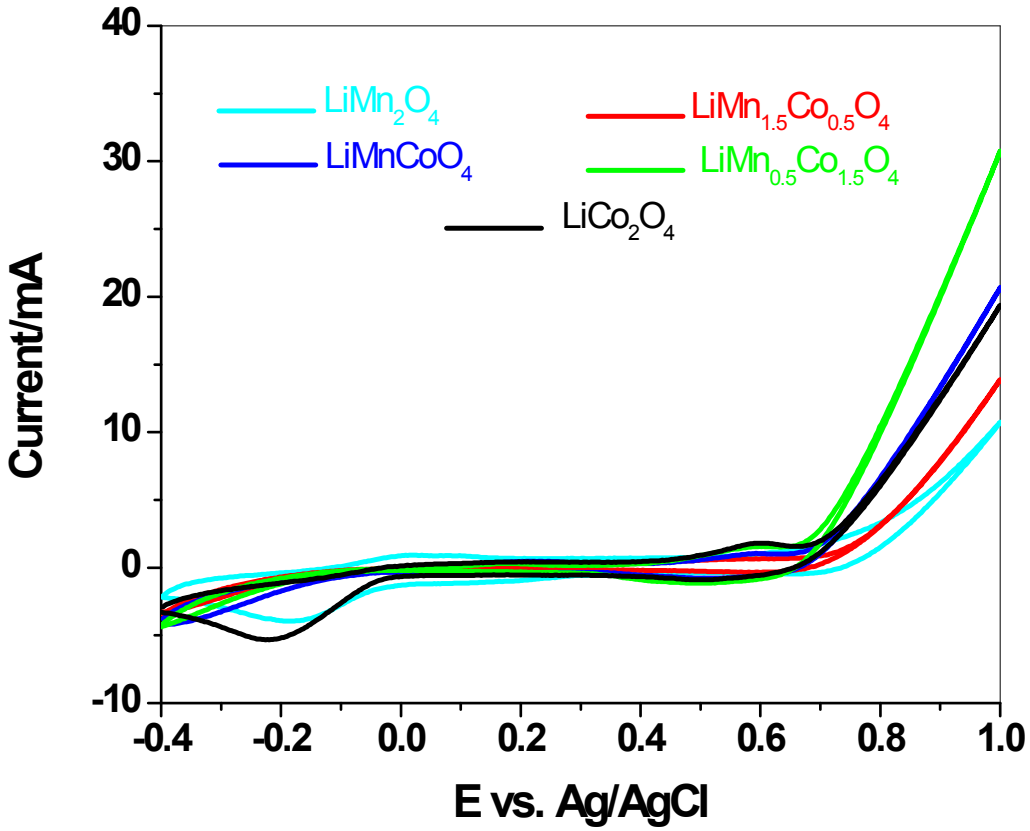

Figure S13. The IR compensated CV data for different compositions showing water oxidation.

Table S1. A summary of electrochemical properties of lithium metalates and some of the most studied mixed metal oxides.

Compounds	pH	Tafel Slope (mV dec^{-1})	η_{1mA} (mV)	η_{10mA} (mV)	Mass activity At 400 mV, (A g^{-1})	Reference
$LiCoO_2$	13	48	-	-	-	[1]
De-$LiCoO_2$	13	50	-	-	-	[1]
De-$LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$	13	48	-	-	-	[1]
LT-$LiCoO_2$	14	48	-	430	5.24	[2]
$LiCO_2$ nanosheets	13	70	-	530	-	[3]
De-$LiCO_2$ nanosheets	13	56	-	500	-	[3]
$LiCO_2$ nanoparticles	13	51	-	510	-	[3]
De-$LiCO_2$ nanoparticles	13	57	-	390	-	[3]
$LiMn_2O_4$-carbon composite	13				10 (at ~500 mV)	[4]
$LiMn_2O_4$	14	140	550	-	1.1	[5]
$LiMn_{1.5}Co_{0.5}O_4$	14	150	420	-	2.3	[5]
$LiMnCoO_4$	14	120	410	530	2.76	[5]
$LiMn_{0.5}Co_{1.5}O_4$	14	60	370	440	8.8	[5]
$LiCoO_2$	14	50	370	410	30	[5]
$LiNi_{0.9}Co_{0.1}O_2$	14				~25[a]	
$Li_{1.03}Ni_{0.66}Co_{0.21}Fe_{0.10}O_{1.95}$					~100[a]	
$LiMn_2O_4$	13.6	**124**	**417**	**541**	**8.1**	This study
$LiMn_{1.5}Co_{0.5}O_4$	13.6	**67**	**300**	**367**	**197**	This study
$LiMnCoO_4$	13.6	**64**	**281**	**345**	**556**	This study
$LiMn_{0.5}Co_{1.5}O_4$	13.6	**66**	**284**	**350**	**409**	This study
$LiCoO_2$	13.6	**64**	**280**	**344**	**901**	This study
$Co_{2.25}Cr_{0.75}O_4$	14	60	~290	350	10.5[b]	[6]
MnO_x	14	49	514	-	1.8[c]	[7]
CoO_x	14	42	405	-	15[c]	[7]
$Ni_{0.75}Co_{0.25}O_x$	14	33	312	-	452[c]	[7]
$Ni_{0.9}Fe_{0.1}O_x$	14	30	297	-	1065[c]	[7]

[a,b] The mass activities are recorded at a) η = 379 mV , b) η = 350 mV, and c) η = 300 mV.

References

1 Z. Lu, H. Wang, D. Kong, K. Yan, P. Hsu, G. Zheng, H. Yao, Z. Liang, X. Sun and Y. Cui, *Nat. Commun.*, 2014, **5**, 1.

2 G. Gardner, J. Al-Sharab, N. Danilovic, Y. B. Go, K. E. Ayers, M. Greenblatt and G. C. Dismukes, *Energy Environ. Sci.*, 2016, **9**, 184.

3 Z. Lu, G. Chen, Y. Li, H. Wang, J. Xie, L. Liao, C. Liu, Y. Liu, T. Wu, Y. Li, A. C. Luntz, M. Bajdich and Y. Cui, *J. Am. Chem. Soc.*, 2017, **139**, 6270.

4 L. Köhler, M. Ebrahimizadeh Abrishami, V. Roddatis, J. Geppert and M. Risch, *ChemSusChem*, 2017, **10**, 4479.

5 C. W. Cady, G. Gardner, Z. O. Maron, M. Retuerto, Y. B. Go, S. Segan, M. Greenblatt and G. C. Dismukes, *ACS Catal.*, 2015, **5**, 3403.

6 C.-C. Lin, C. C. L. McCrory, *ACS Catal.*, 2017, **7**, 443.

7 L. Trotochaud, J. K. Ranney, K. N. Williams, S. W. Boettcher, *J. Am. Chem. Soc.* 2012, **134**, 17253.