LOMONOSOV MOSCOW STATE UNIVERSITY

Laboratory of Inorganic Crystal Chemistry

Mn (III) - containing spinels as ORR catalysts in an alkaline medium

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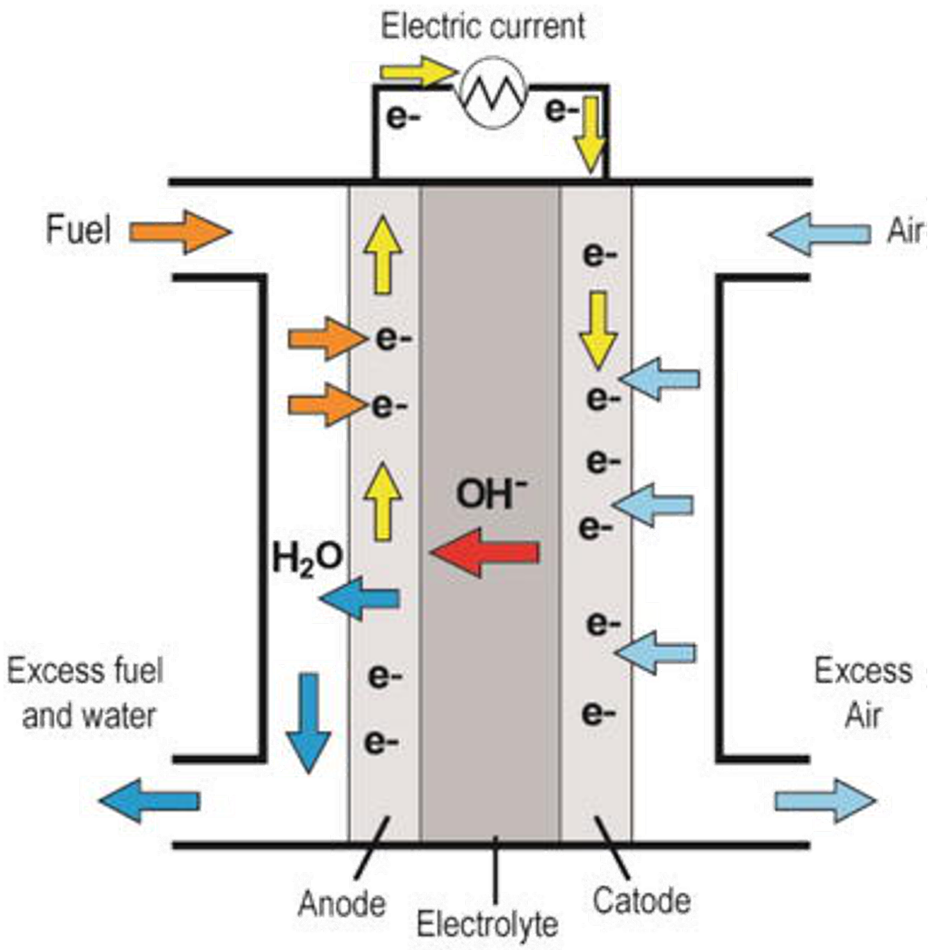
Alkaline fuel cell

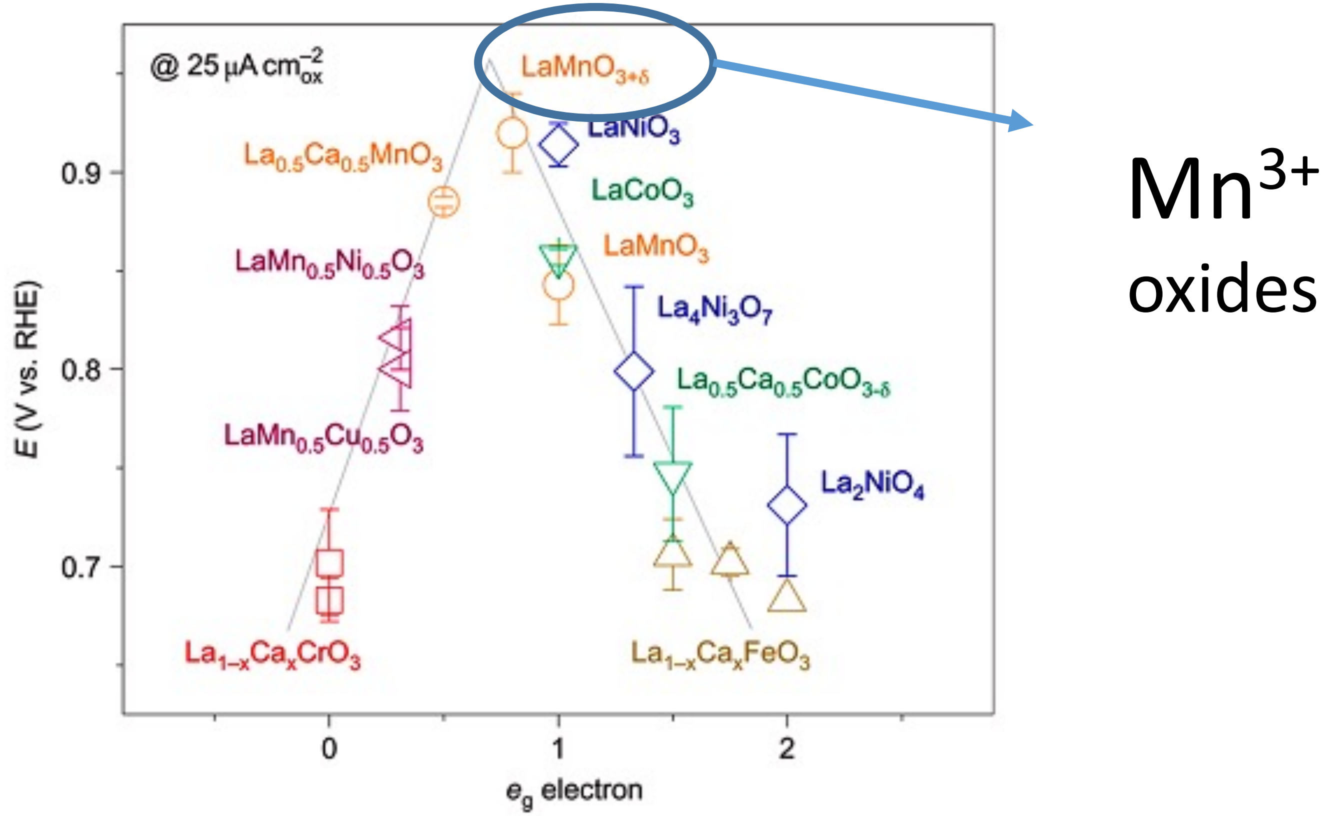


Alkaline fuel cell diagram

Electrode Reactions:

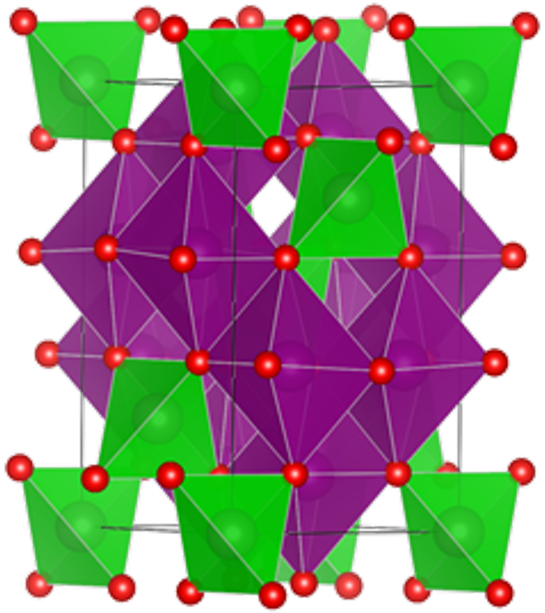
Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ oxygen reduction reaction (ORR)

Anode: $4OH^- + 2H_2 = 4H_2O + 4\bar{e}$ fuel oxidation reaction



Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries, Jin Suntivich and etc// Nature Chemistry, vol 3, p. 546-550

Objects



Structure of tetragonal spinel AB_2O_4

Mn^{2+}	0.80 Å
Mg^{2+}	0.71 Å
Li^{+}	0.73 Å
Cd^{2+}	0.92 Å

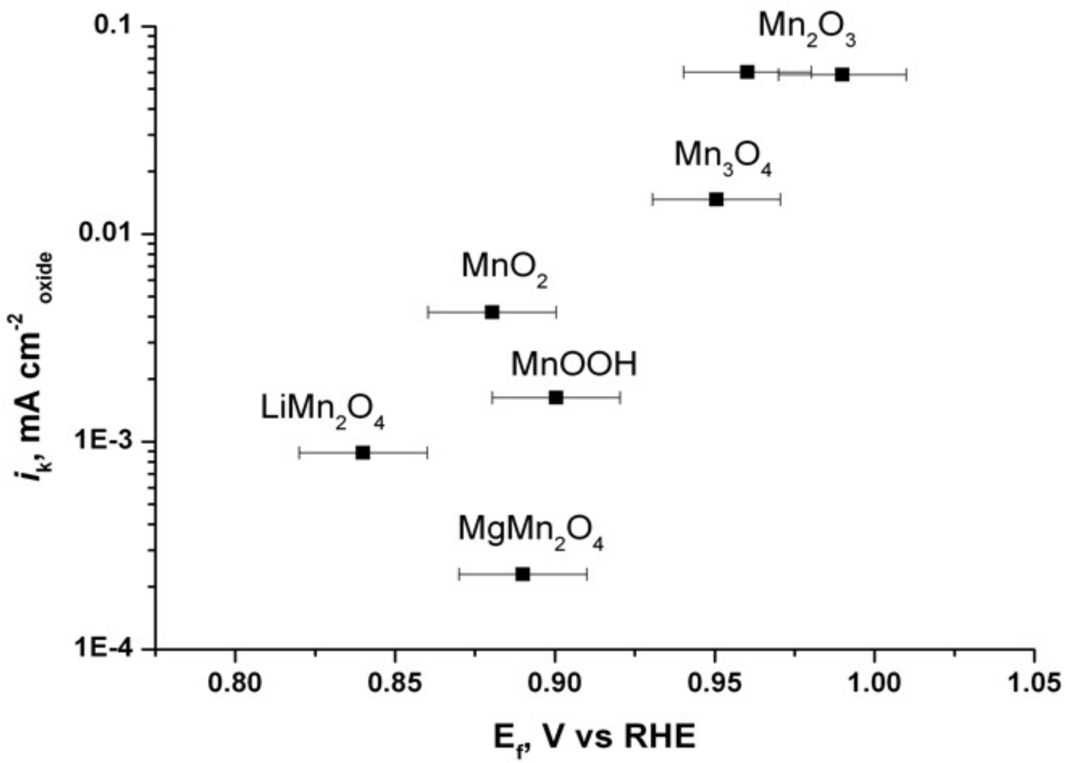
Ion radii of cations at CN = 4

$Mn^{2+}Mn^{+3}{}_2O_4$

$Mg^{2+}Mn^{+3}{}_2O_4$

$LiMn^{+3.5}{}_2O_4$

$Cd^{2+}Mn^{+3}{}_2O_4$



Rationalizing the Influence of the Mn(IV)/Mn(III) Red-Ox Transition on the Electrocatalytic Activity of Manganese Oxides in the Oxygen Reduction Reaction, Anna S. Ryabova and etc // Electrochimica Acta 187 (2016) 161–172

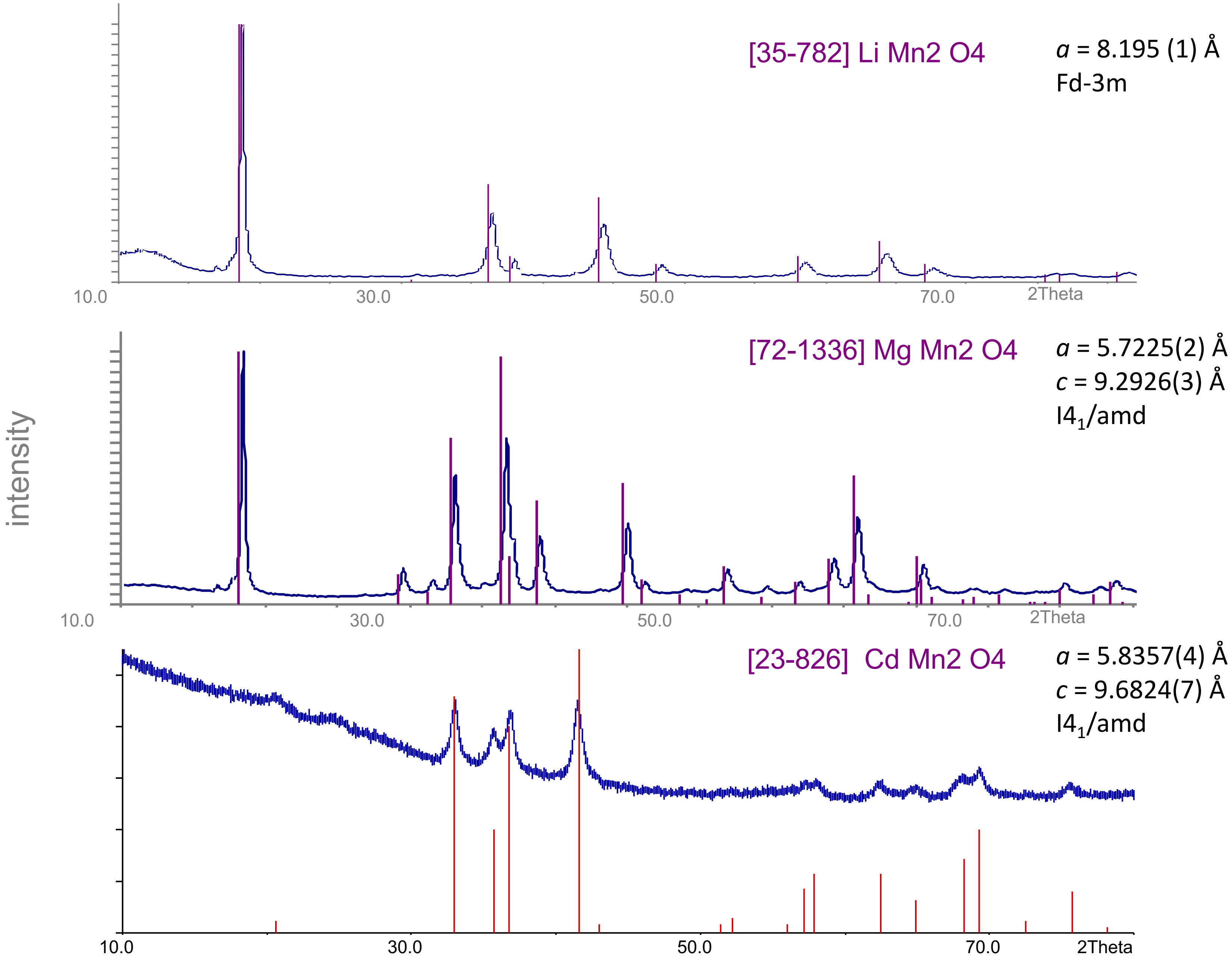
Synthesis of AMn_2O_4, A=Li, Mg, Cd

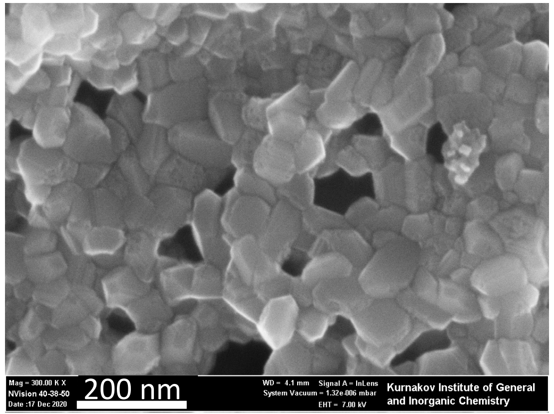
$$LiNO_3 + 2\,Mn(NO_3)_2 \rightarrow \text{solution} \xrightarrow[\text{gas-burner}]{\text{PVA + citric acid}} \xrightarrow[\text{300 °C / 12 hours}]{\text{Annealing Air}} \mathbf{LiMn_2O_4}$$

$$Mg(NO_3)_2 + 2\,Mn(NO_3)_2 \rightarrow \text{solution} \xrightarrow[\text{gas-burner}]{\text{PVA + citric acid}} \xrightarrow[\text{600 °C / 6 hours}]{\text{Annealing Air}} \mathbf{MgMn_2O_4}$$

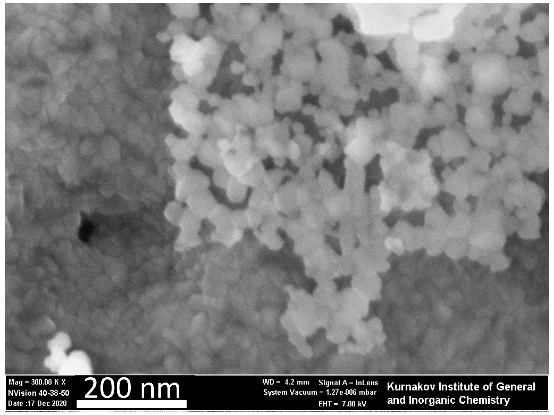
$$Cd(NO_3)_2 + 2\,Mn(NO_3)_2 \rightarrow \text{solution} \xrightarrow[\text{0.8M NaOH}]{\text{stream } O_2} \xrightarrow{\text{sludge drying}} \xrightarrow[\text{300 °C / 12 hours}]{\text{Annealing Air}} \mathbf{CdMn_2O_4}$$

X-ray phase analysis and micrographs

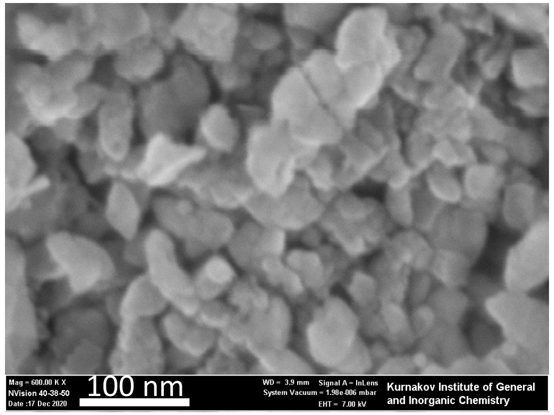




$LiMn_2O_4$, S (BET) = **21** $м^2$/г



$MgMn_2O_4$, S (BET) = **22** $м^2$/г



$CdMn_2O_4$, S (BET) = **39** $м^2$/г

Electrochemical measurements

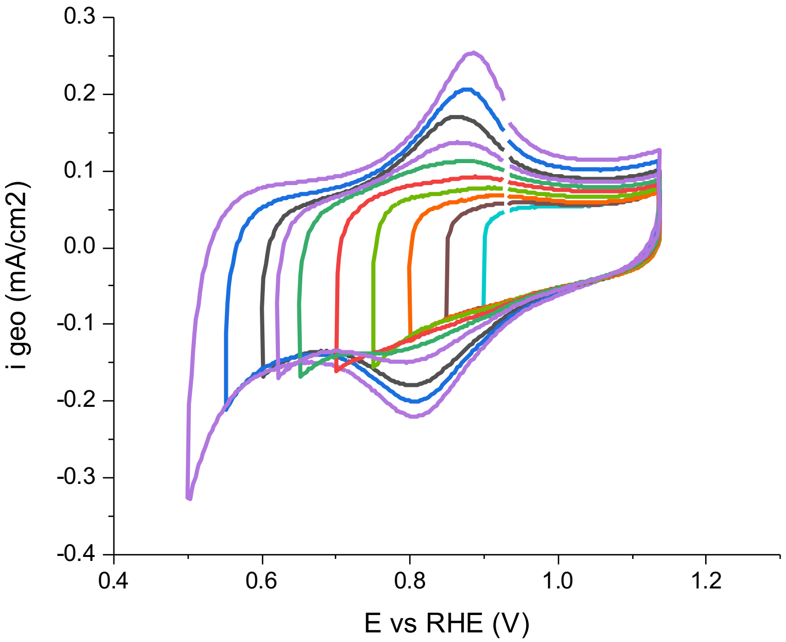
Electrochemical cycling with a gradual decrease of the cathode limit potential.

<u>Electrochemical study:</u>

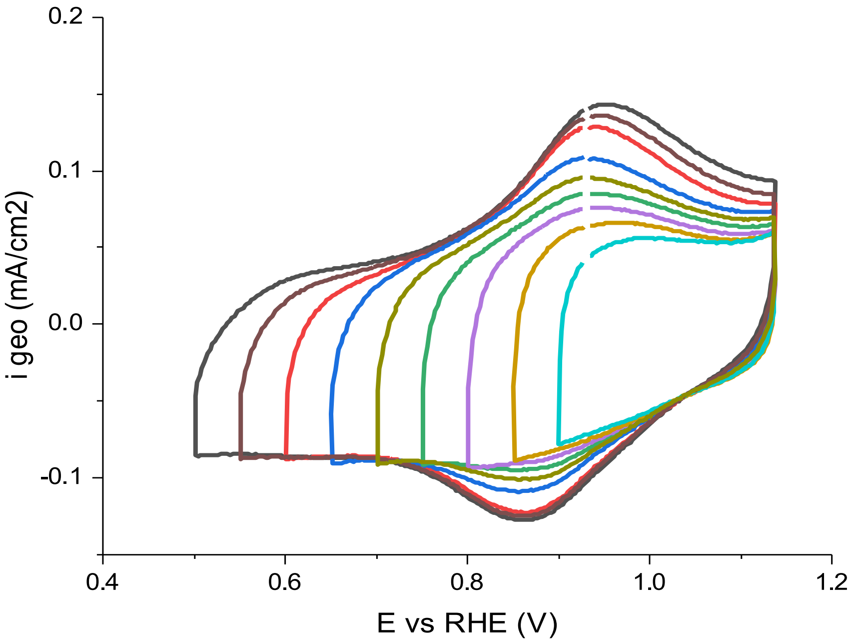
Electrode: composite (carbon (91 µg /cm^2) + $CdMn_2O_4$ (91 µg / cm^2)), working electrode - RDE, counter electrode - Pt, reference electrode - Hg / HgO.

Measurement in oxygen free solution of 1 M NaOH. Sweep rate 10 mV / s.

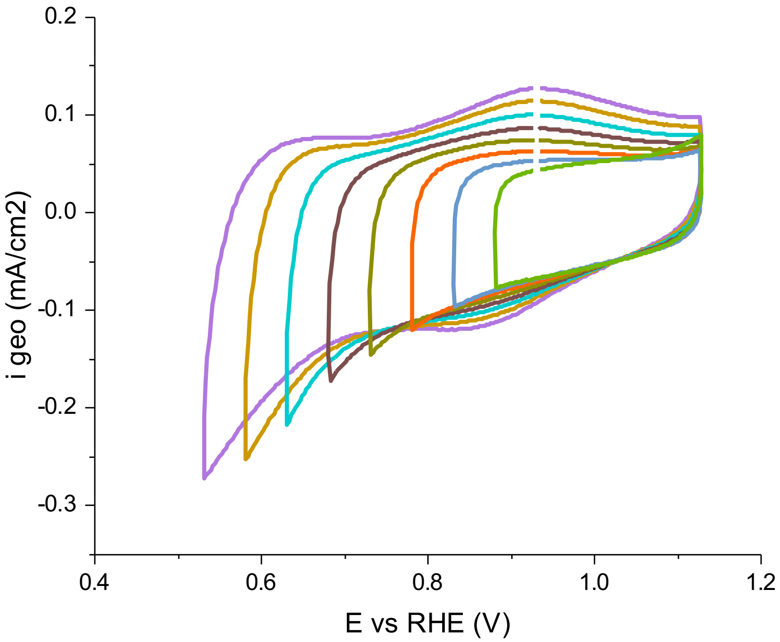
$LiMn_2O_4$



$MgMn_2O_4$



$CdMn_2O_4$



Oxygen reduction reaction

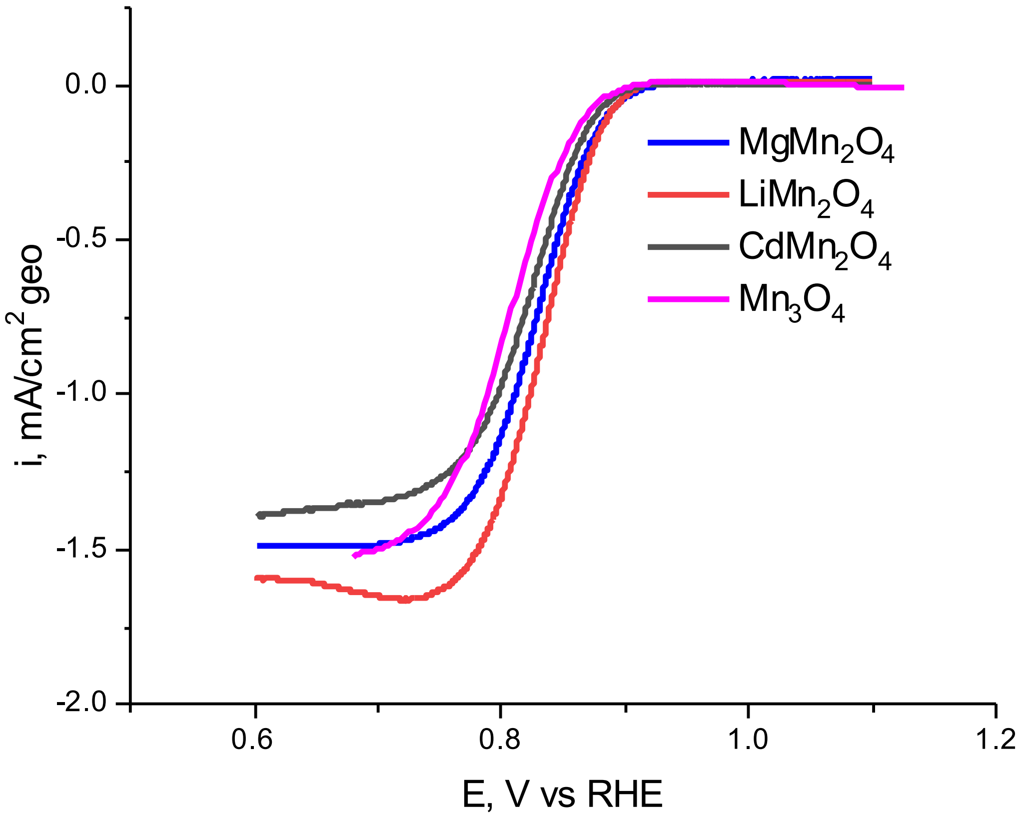
Electrochemical study:

Measurement in a saturated O_2 solution of 1 M NaOH.

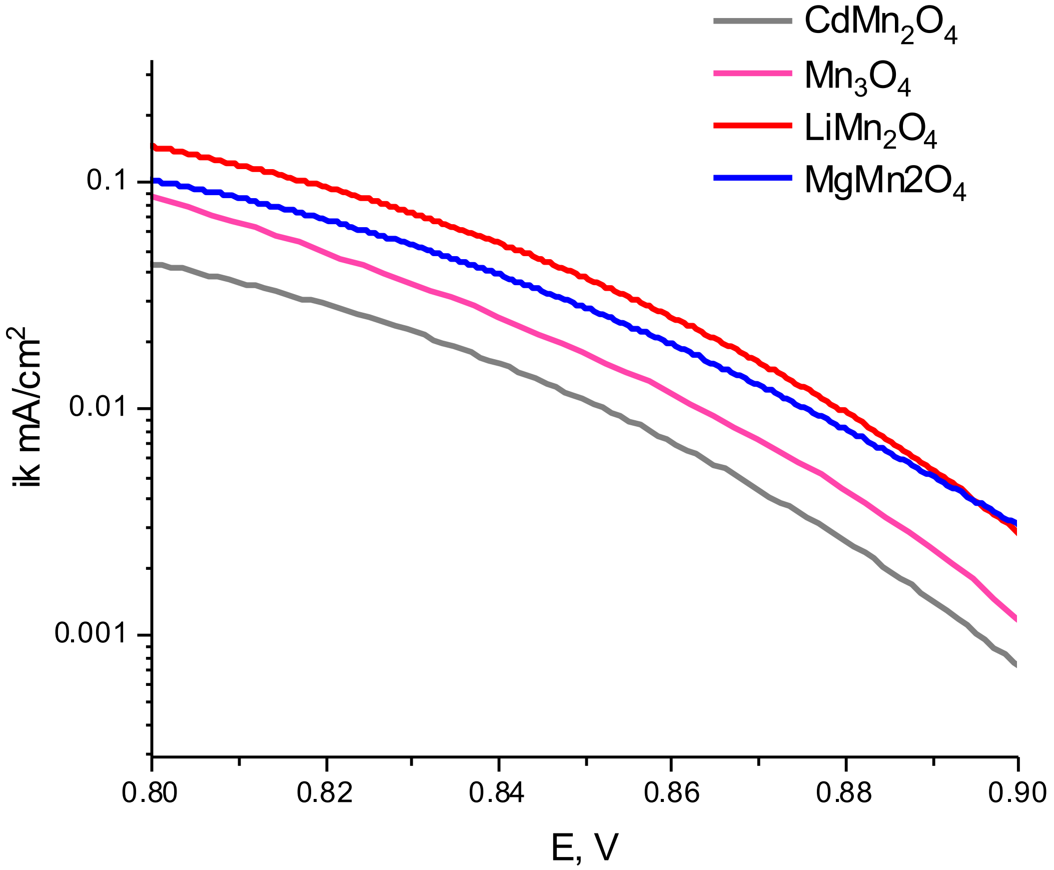
Sweep speed 10 mV / s. Rotational speeds 400, 900, 1600, 2500 rpm.

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L}$$

900 rpm polarization curves

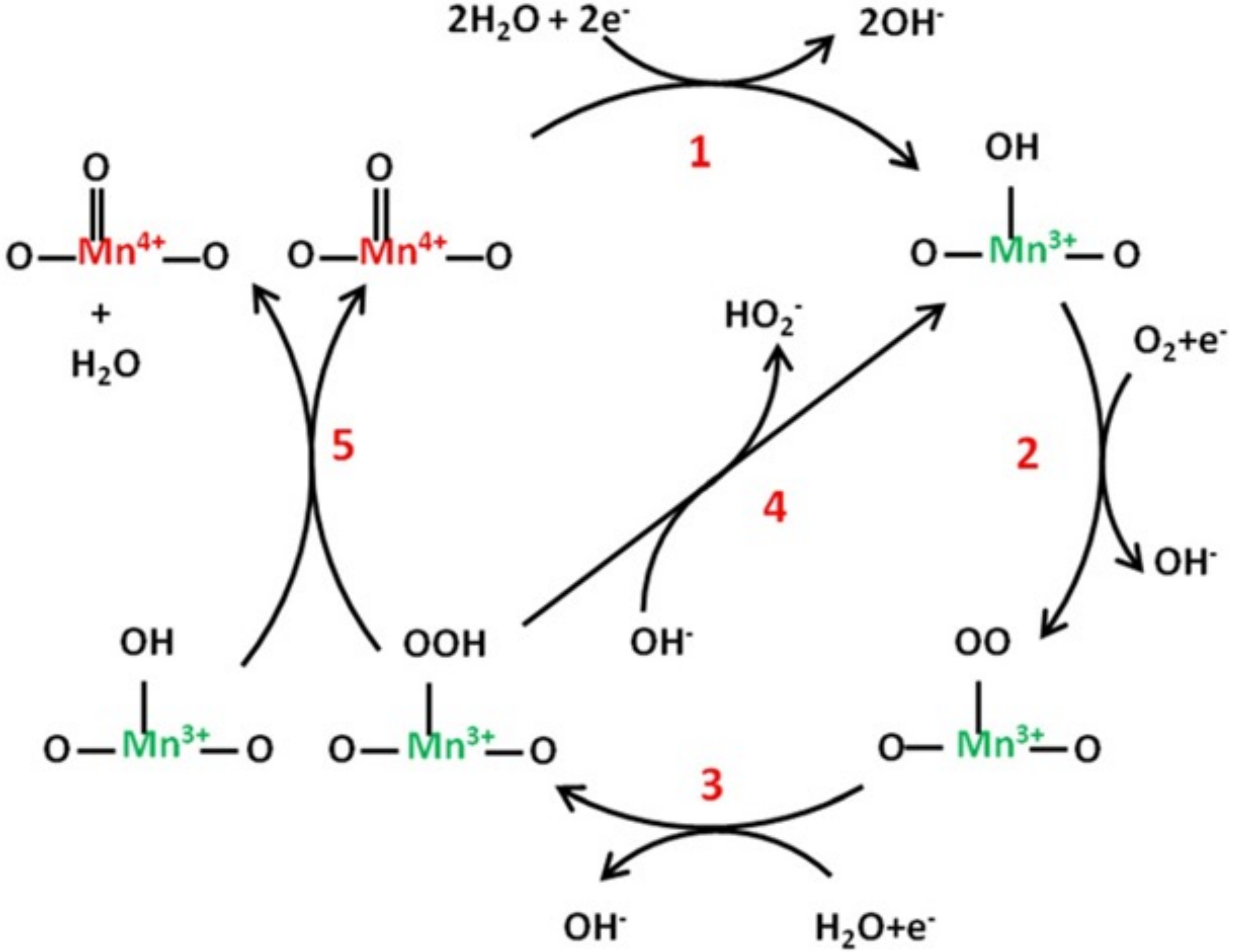


Tafel dependencies

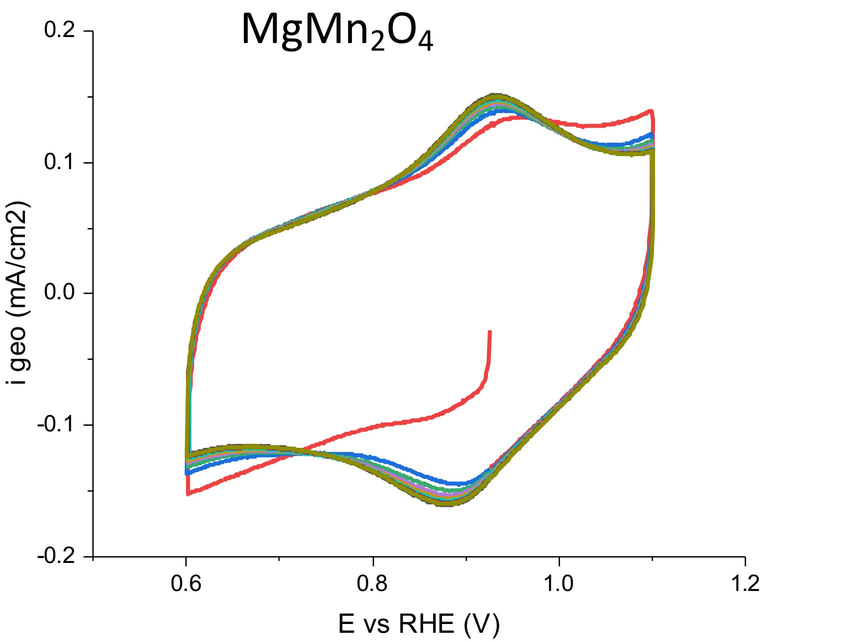


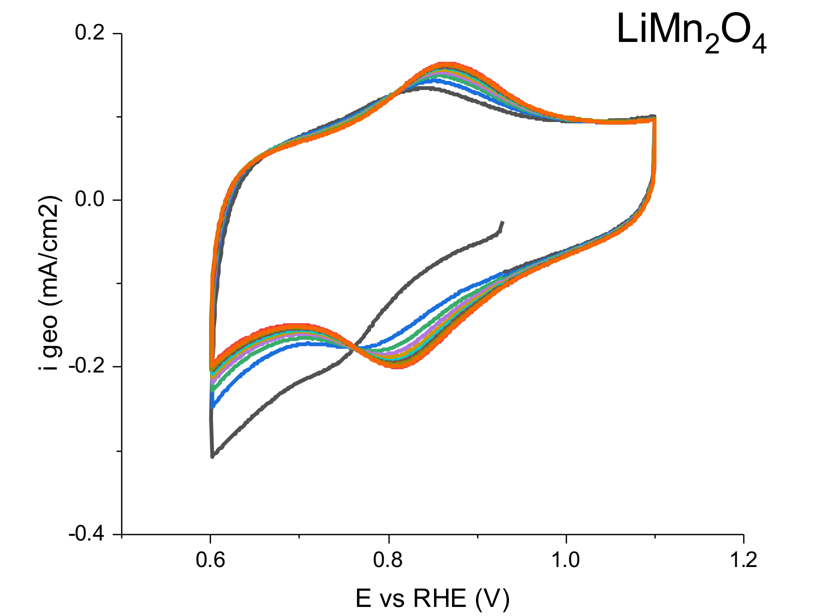
Results

- Oxides of the AMn_2O_4, A = Li, Mg, Cd series exhibit catalytic activity in the oxygen reduction reaction. $LiMn_2O_4$ has the highest activity among the studied compounds with a spinel structure.
- $LiMn_2O_4$ and $CdMn_2O_4$ demonstrate irreversible surface changes during cycling in a wide range of potentials.
- Spinel $MgMn_2O_4$ is one of the promising oxide catalysts, since it has been found to be most stable in an alkaline medium both during electrochemical cycling and in direct contact with the supporting electrolyte.



2H2O + 2e-
2OH-
1
OH
O—Mn4+—O
O—Mn4+—O
O
O
+
H2O
O—Mn3+—O
HO2-
O2+e-
2
5
4
OH-
OH
OOH
OH-
OO
O—Mn3+—O
O—Mn3+—O
O—Mn3+—O
3
OH-
H2O+e-


$MgMn_2O_4$
i geo (mA/cm2)
E vs RHE (V)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i geo (mA/cm2)
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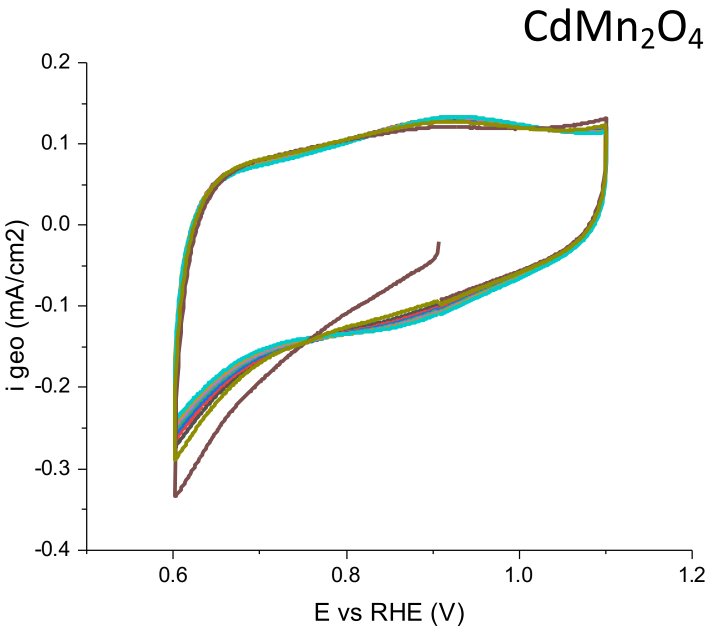
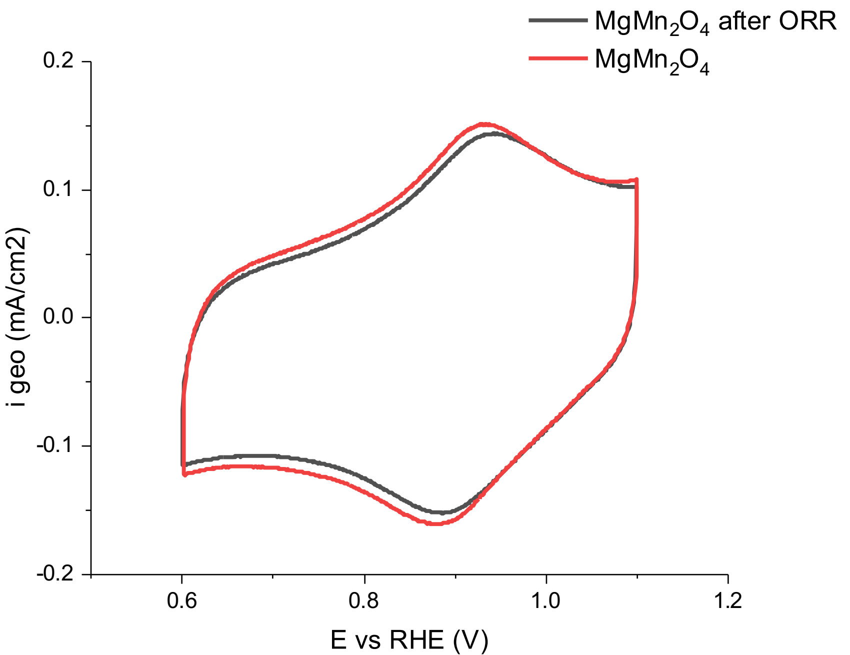
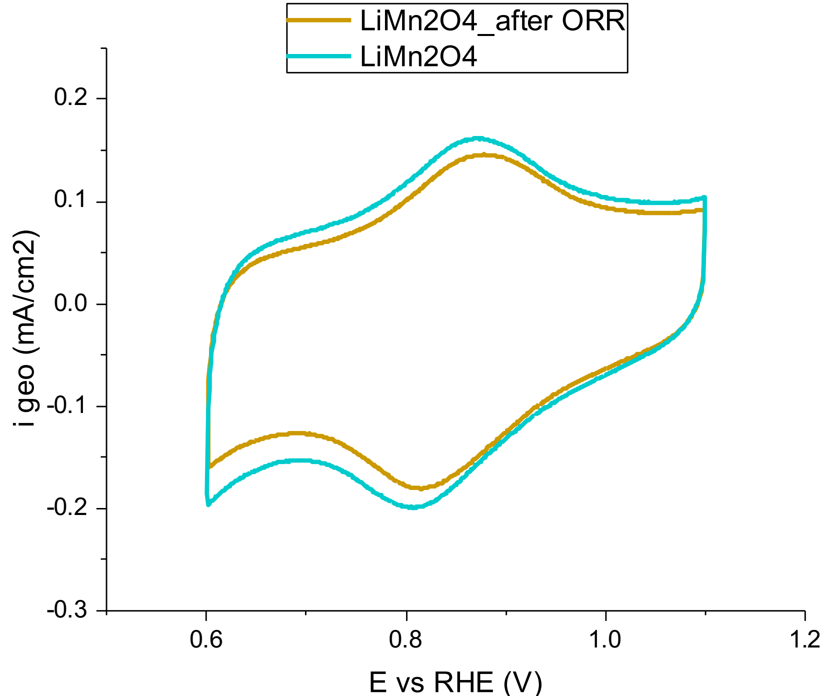
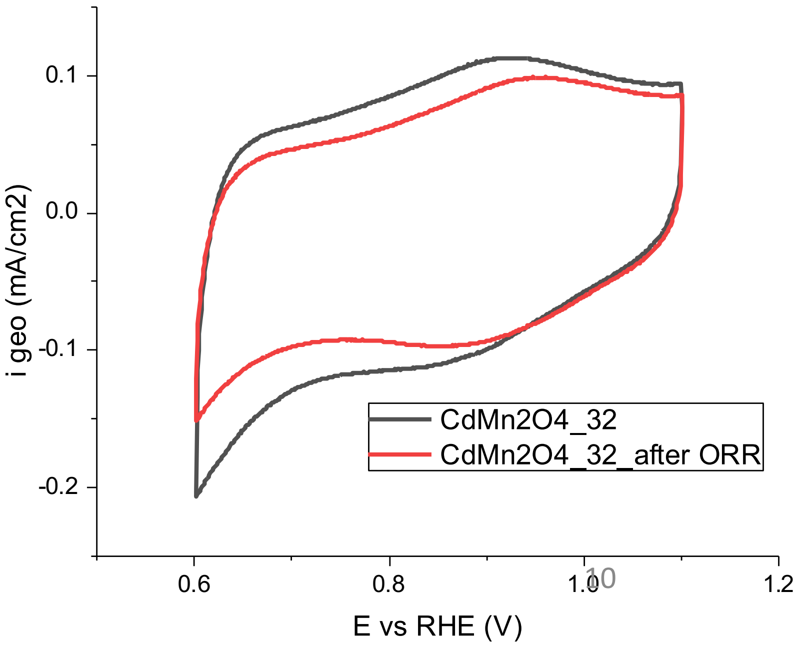
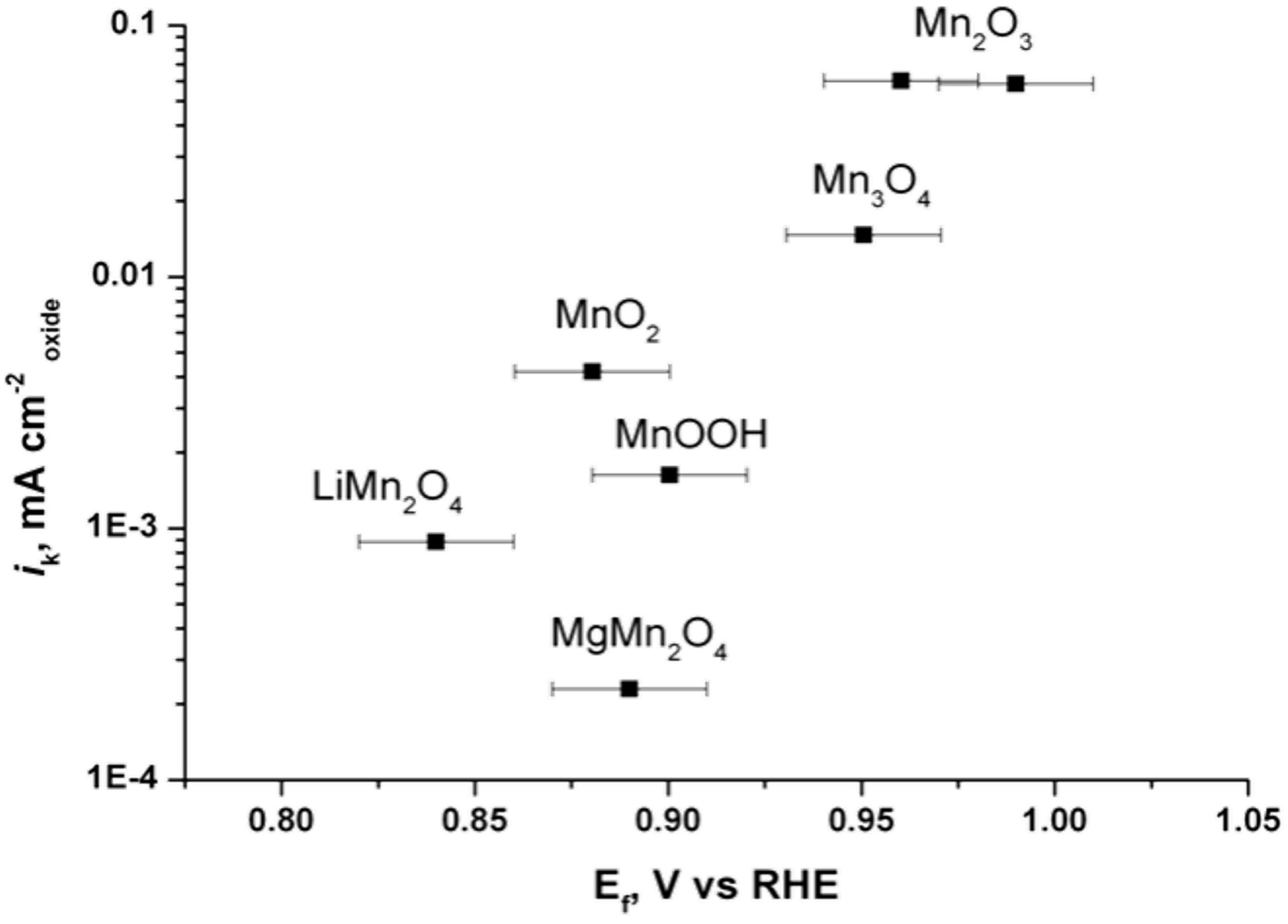

$CdMn_2O_4$
i geo (mA/cm2)
E vs RHE (V)


$MgMn_2O_4$ after ORR
$MgMn_2O_4$
i geo (mA/cm2)
E vs RHE (V)


LiMn2O4_after ORR
LiMn2O4
i geo (mA/cm2)
E vs RHE (V)


CdMn2O4_32
CdMn2O4_32_after ORR
i geo (mA/cm2)
E vs RHE (V)



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