Electronic Supplementary Material (ESI) for Dalton Transactions.

Influence of Fe-clustering in the water oxidation performance of two-dimensional layered double hydroxides

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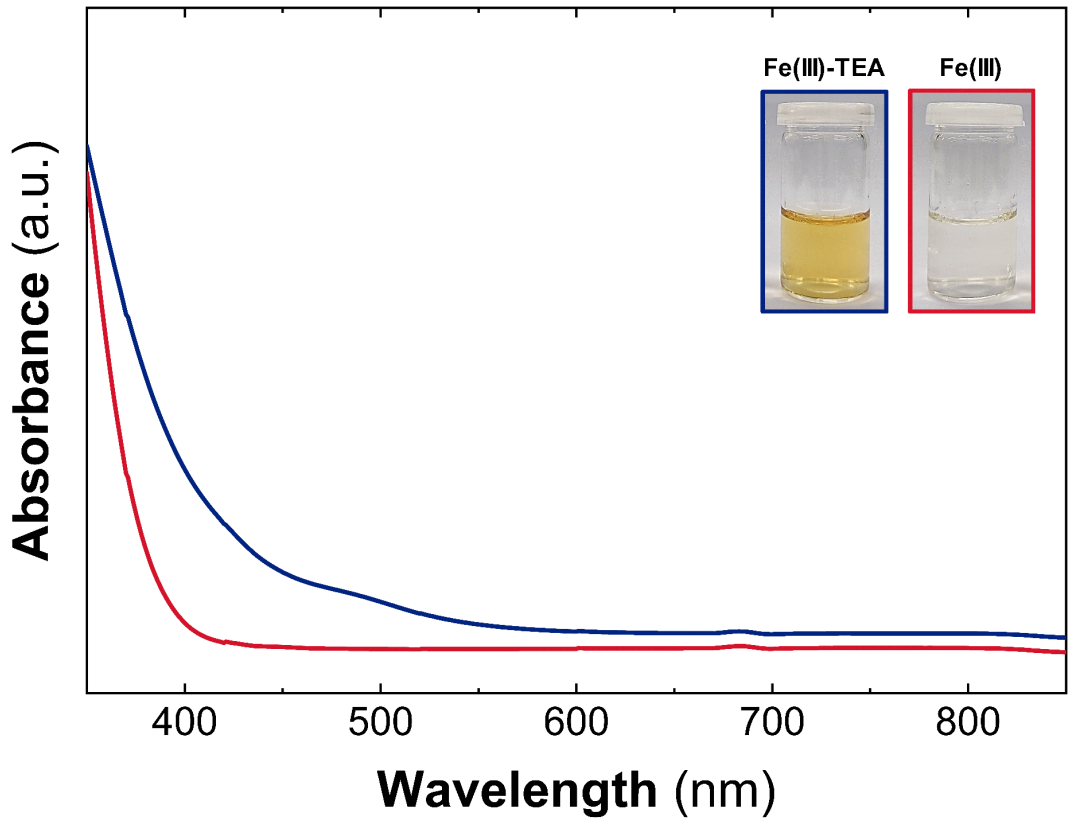

Figure S1. UV-Vis spectra of aqueous solutions containing [Fe(III)] = 5 mM without (red) and with [TEA] = 5 mM (blue).

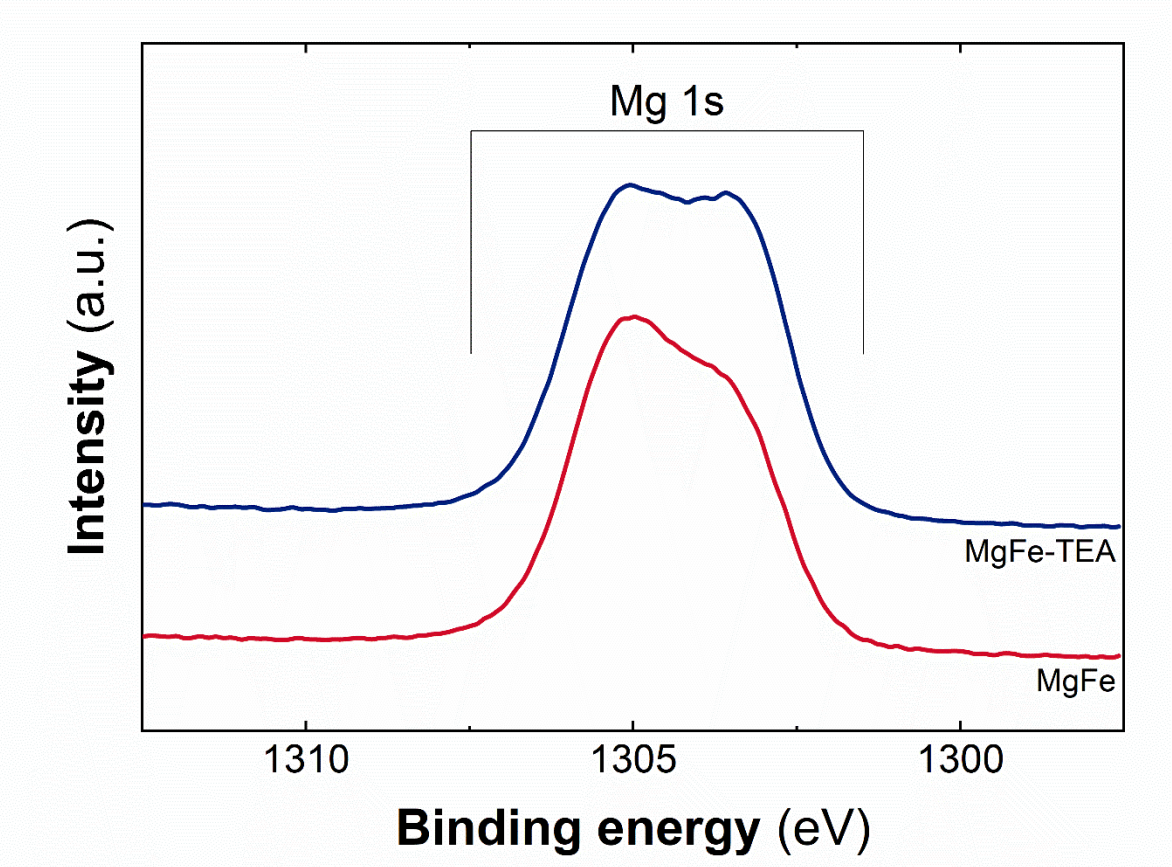

Figure S2. High resolution Mg 1s XPS spectra in the range 1315 – 1295 eV for samples MgFe-TEA (blue) and MgFe (red).

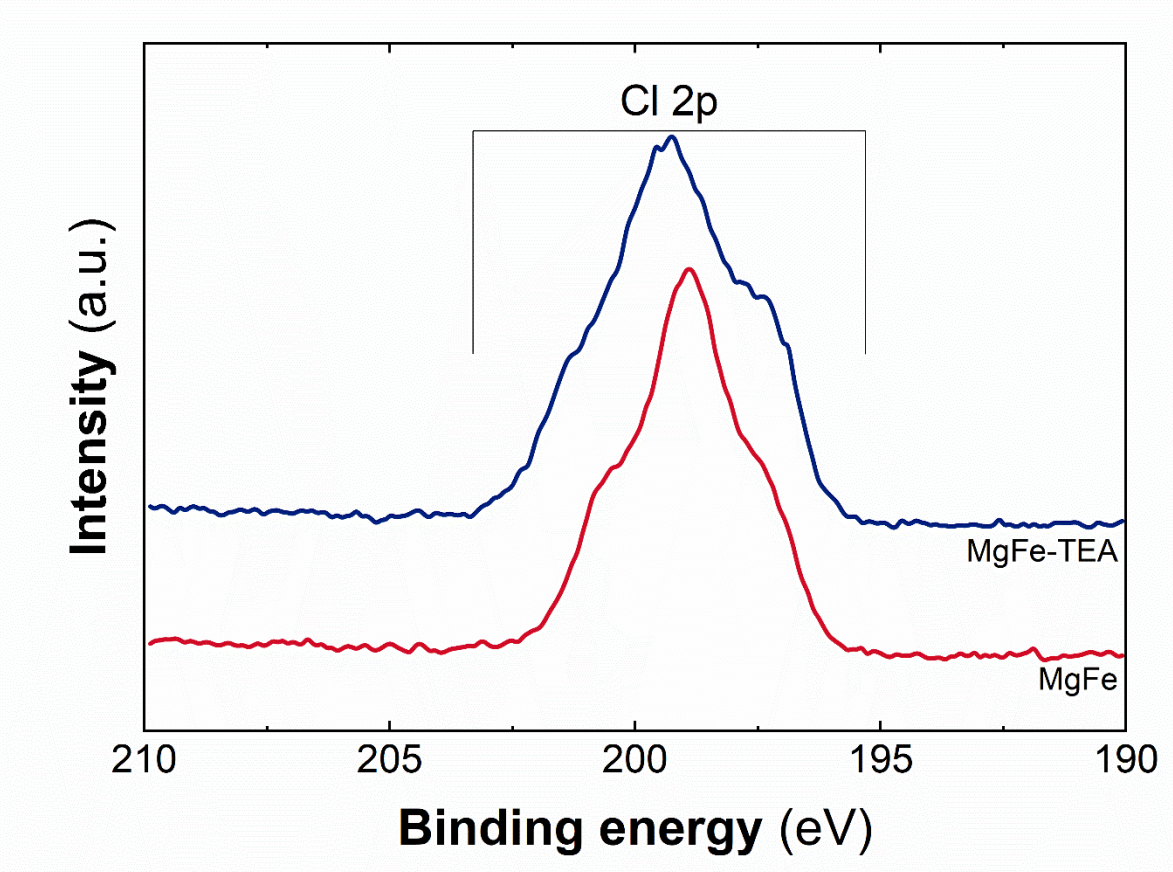

Figure S3. High resolution Cl 2p XPS spectra in the range 210 – 190 eV for samples MgFe-TEA (blue) and MgFe (red).

Table S1. Chemical formula, structural parameters (**d**), crystalline size (*L*), Mg:Fe and Cl:Fe ratios for MgFe and MgFe-TEA LDHs samples.

Sample	**Chemical formula**	$\mathbf{d_{BS}}$ (Å)	$\boldsymbol{L_{001}}$ (nm)	$\mathbf{d_{110}}$ (Å)	$\boldsymbol{L_{110}}$ (nm)	**Mg:Fe**			**Cl:Fe**	
						XPS	EDS	ICP-MS	XPS	EDS
MgFe-TEA	$Mg_2Fe(OH)_6Cl_{0.6}(CO_3)_{0.2} \cdot 0.5(H_2O)$	8.06	26.4	1.56	26.2	1.8	2.0	2.1	0.7	0.6
MgFe	$Mg_2Fe(OH)_6Cl_{0.6}(CO_3)_{0.2} \cdot 0.5(H_2O)$	8.06	18.5	1.56	27.2	1.7	1.9	2.1	0.7	0.6

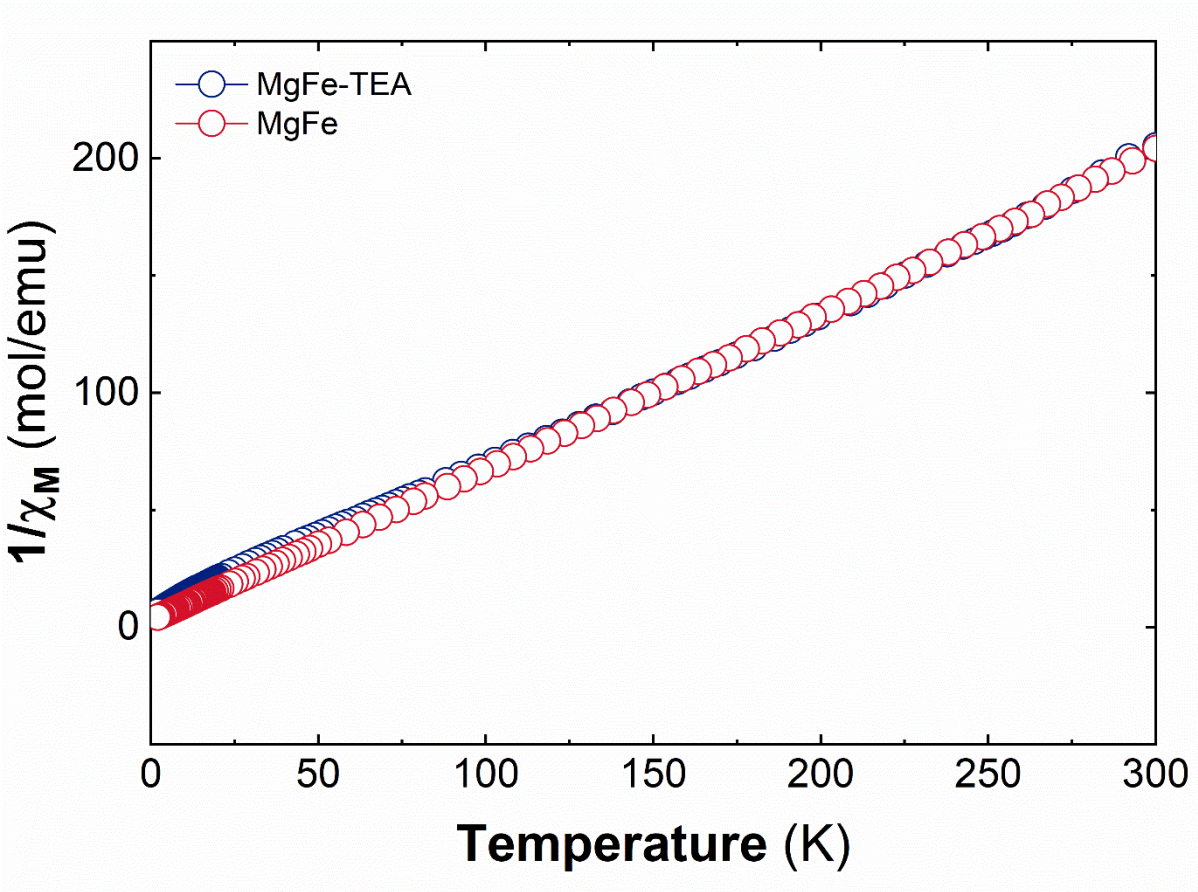

Figure S4. Fitting of the $1/\chi_M$ to a Curie–Weiss law for samples MgFe-TEA (blue) and MgFe (red).

Table S2. Magnetic parameters of MgFe-TEA and MgFe samples.

Sample	$C_{spin\text{-}only}$ (emu·K/mol)	C_{exp} (emu·K/mol)	Θ (K)
MgFe-TEA	1.44	1.44	-8.13
MgFe	1.44	1.45	-5.49

$C_{spin\text{-}only}$**:** expected spin-only value of the Curie constant, calculated as a diluted combination of Mg^{2+} (S= 0) and Fe^{3+} (S = 5/2).

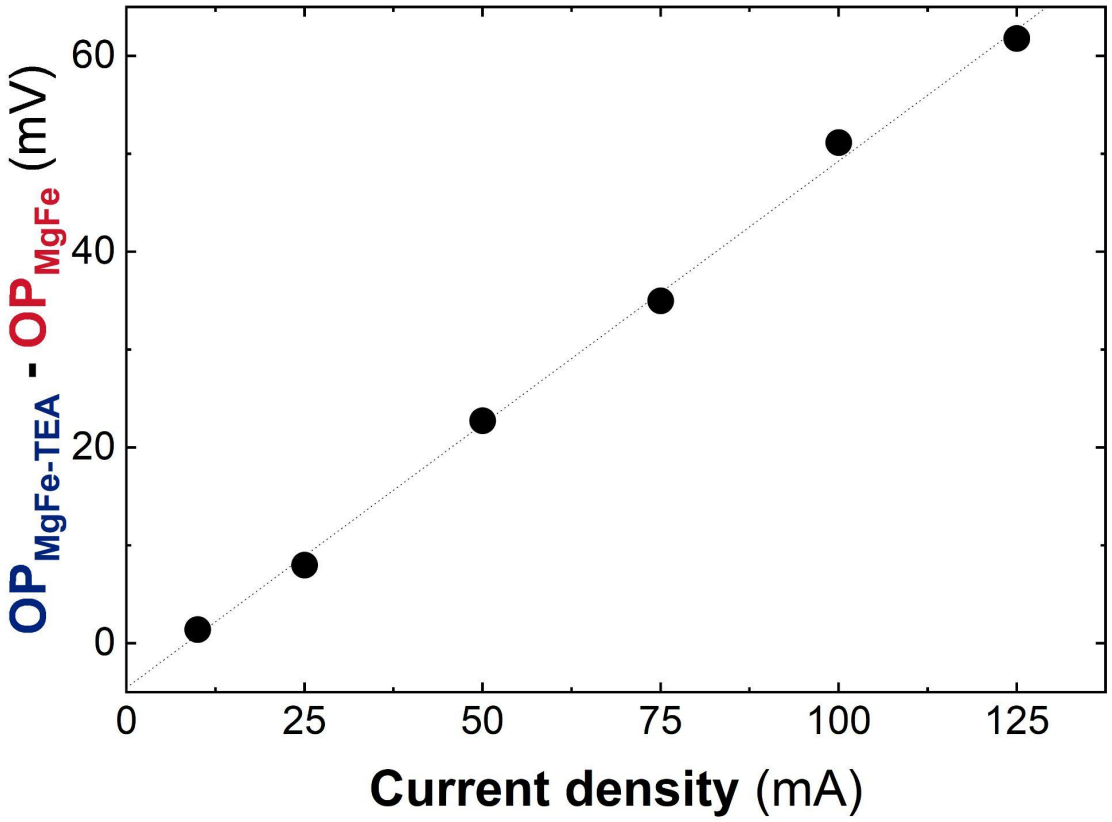

Figure S5. Differences in the overpotential for both samples ($OP_{MgFe} - OP_{MgFe\text{-}TEA}$) as a function of the current density.

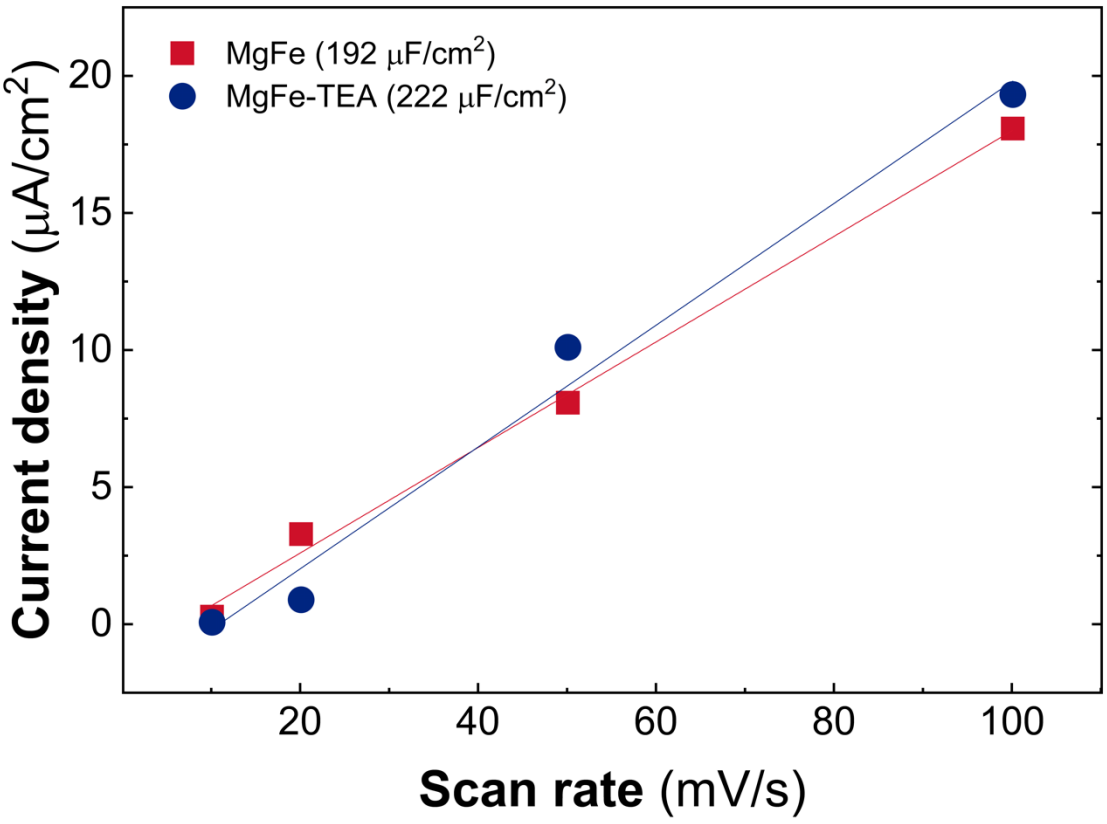

Figure S6. Electrochemical surface area (ECSA) of the MgFe-LDH samples calculated from CVs performed in a non-faradaic region at different scan rates.

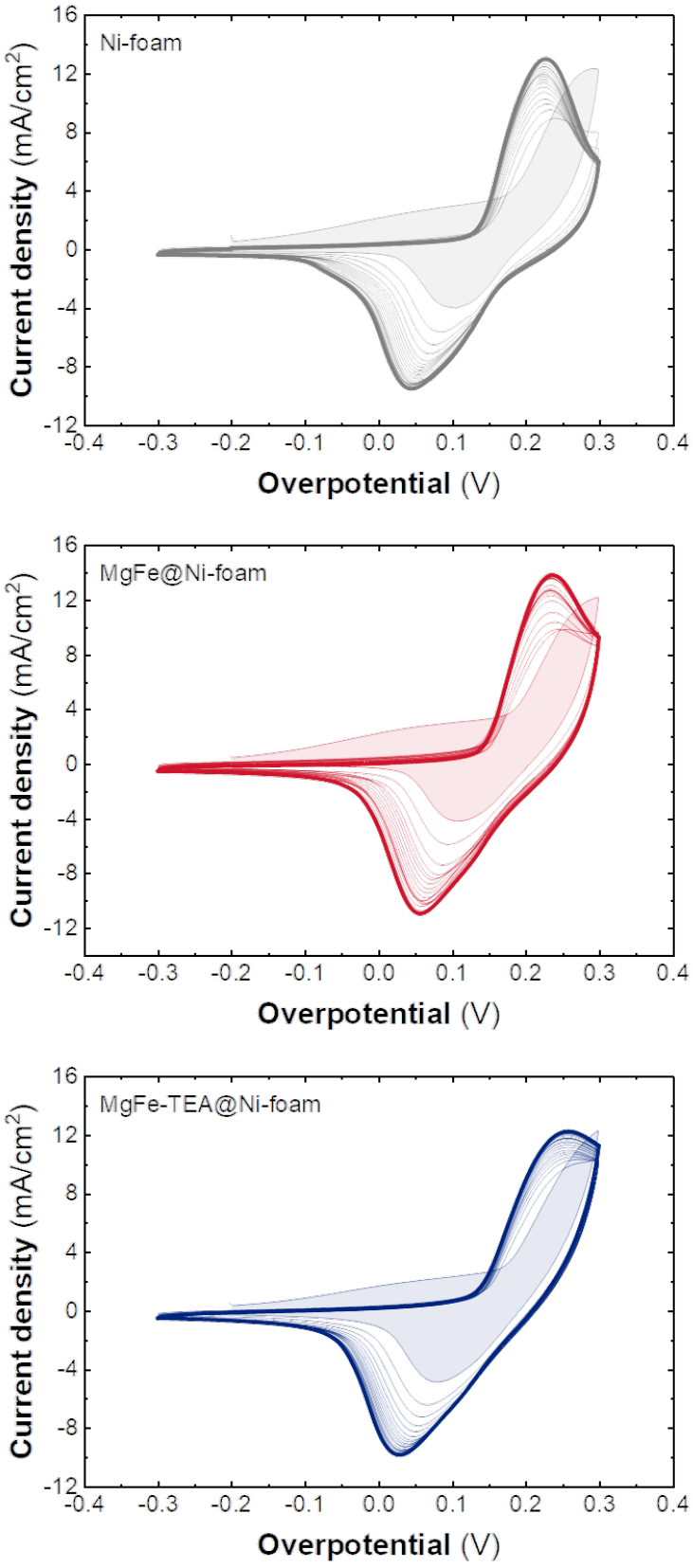

Figure S7. Electrocatalysts activation process performed as CVs recorded at 100 mV/s during 20 cycles: first cycle (shading cycle) and last cycle (thick line).