SUPPORTING INFORMATION

Entropy-Driven Mechanisms in P2-Type Layered Oxide Cathodes for Sodium-Ion Batteries: New Insights from First-Principles and Electrochemical Analysis

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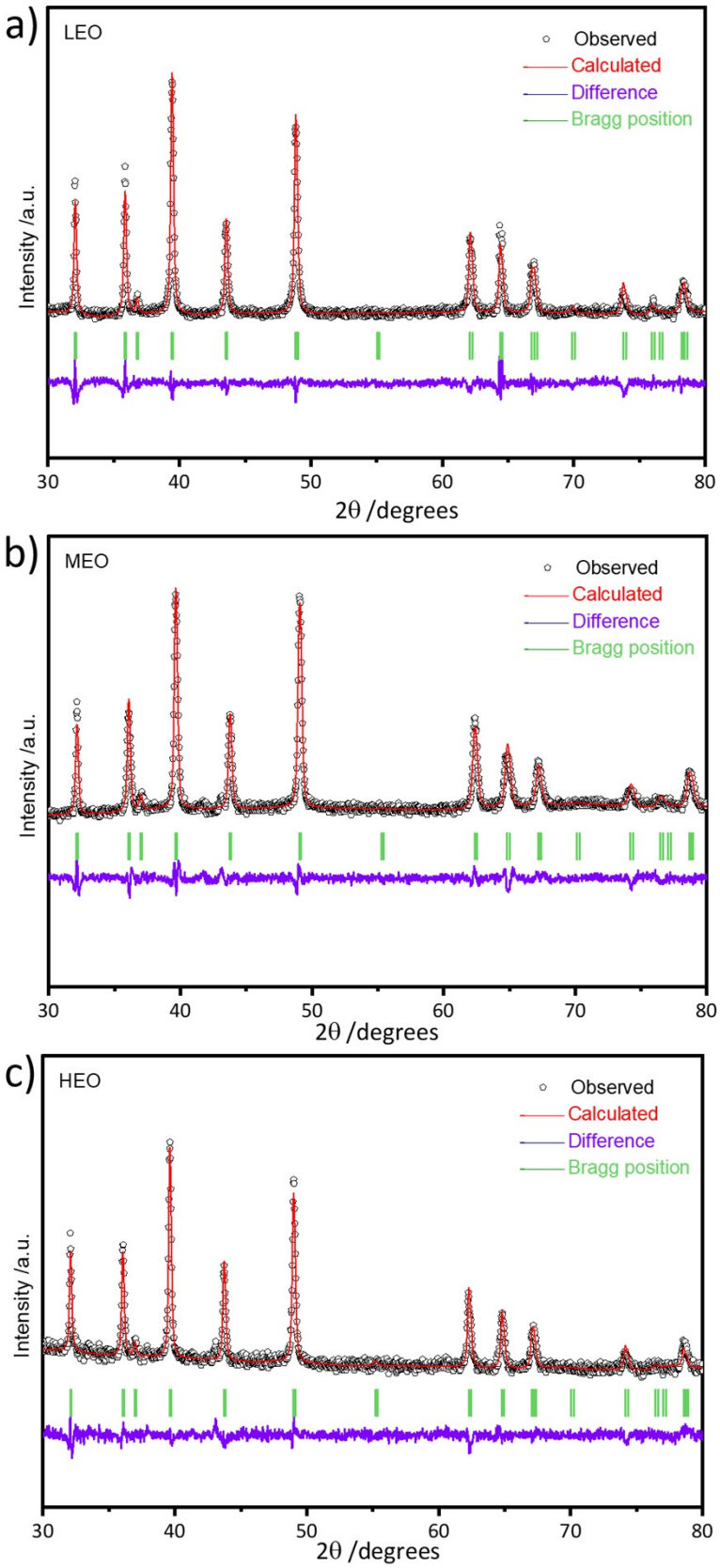


Figure S1. *XRD patterns and Rietveld refinement results for* ***(a)*** *LEO (unweighted profile factor* R_p*=2.6%),* ***(b)*** *MEO (*R_p*=2.1%), and* ***(c)*** *HEO (*R_p*=1.6%).*

Table S1. *Results of Rietveld refinement for the three samples, including lattice parameters (a, b, c), cell volume V, angles (α, β, γ), and unweighted profile factor R_p.*

	a,b (Å)	**c (Å)**	**V (Å^3)**	**α , β**	**γ**	**R_p (%)**
LEO	2.8912	11.1641	80.8198	90°	120°	2.6
MEO	2.8742	11.1385	79.6871	90°	120°	2.1
HEO	2.8757	11.1532	79.8741	90°	120°	1.6

Table S2. *Lattice parameters of the minimum-energy structures for the P2-Na_xMO_2 series in their 8x4x1 supercells as obtained at the PBE+U-D3BJ level of theory.*

	LEO		**MEO**		**HEO**	
x_{Na}	**a,b (Å)**	**c (Å)**	**a,b (Å)**	**c (Å)**	**a,b (Å)**	**c (Å)**
0.68	23.272	11.233	23.097	11.155	23.127	11.169
0.50	23.165	11.181	23.007	11.112	22.808	11.487
0.30	23.097	11.149	23.031	11.123	22.773	11.469
0.12	22.951	11.078	22.927	11.073	22.794	11.480

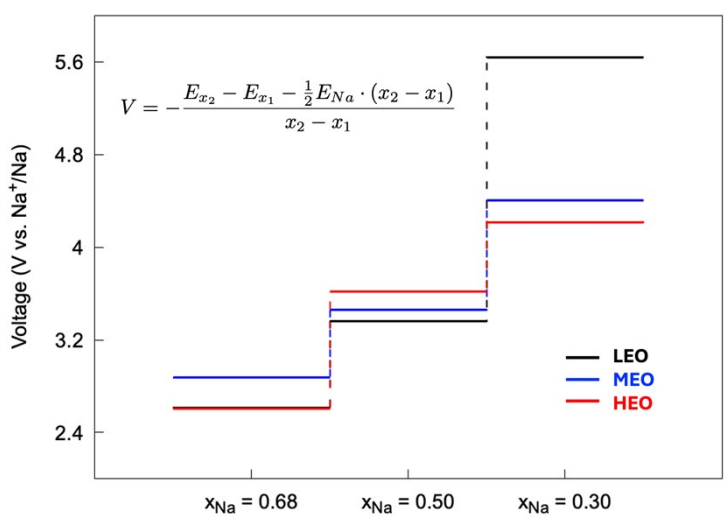


Figure S2. *Capacity-voltage profile of P2-Na_xMO_2 compounds computed at PBE+U-D3BJ level of theory according to the displayed equation. Color legend is shown in the graph.*

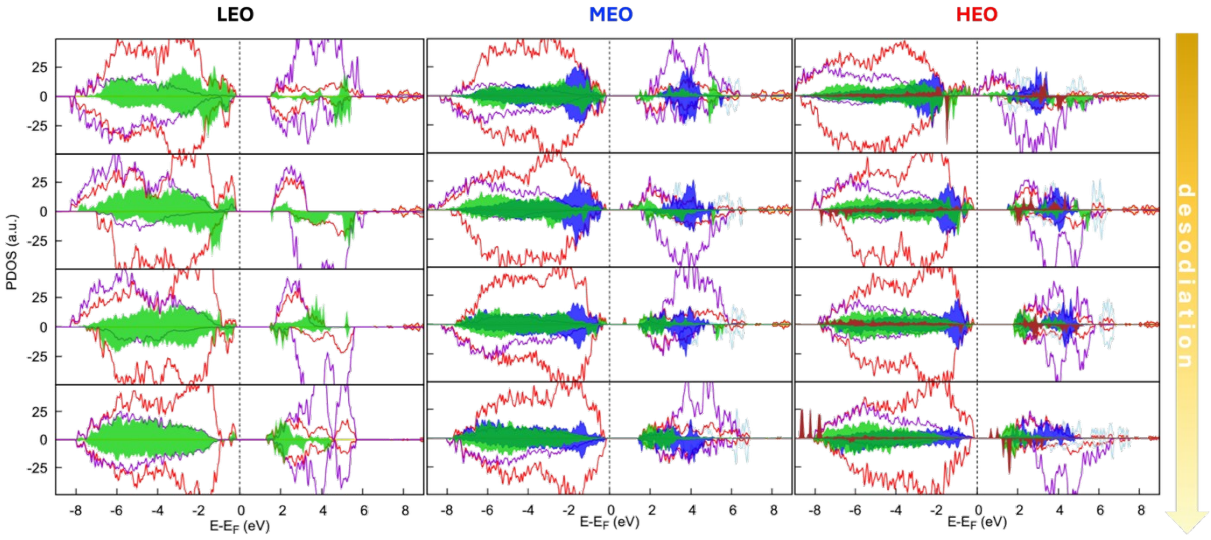


Figure S3. *Atom- and angular momentum-projected density of states (PDOS) of LEO, MEO, and HEO as function of sodiation degree computed at HSE06 level of theory. Color code: Na s states, yellow; Mn d states, violet; Ni d states, green; Co d states, blue; Ti d states, cyan; Mg s states, orange; Al p states, grey; Fe d states, burgundy; O p states, red.*

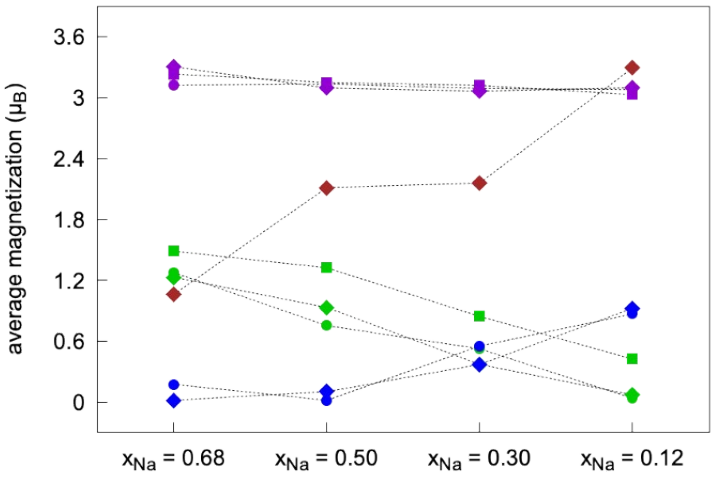


Figure S4. *Average magnetization on Mn, Ni, Co and Fe sublattices in LEO, MEO and HEO as function of sodiation degree computed at HSE06 level of theory. Legend: Mn purple, Ni green, Co blue, Fe brown; LEO squares, MEO circles, HEO diamonds.*

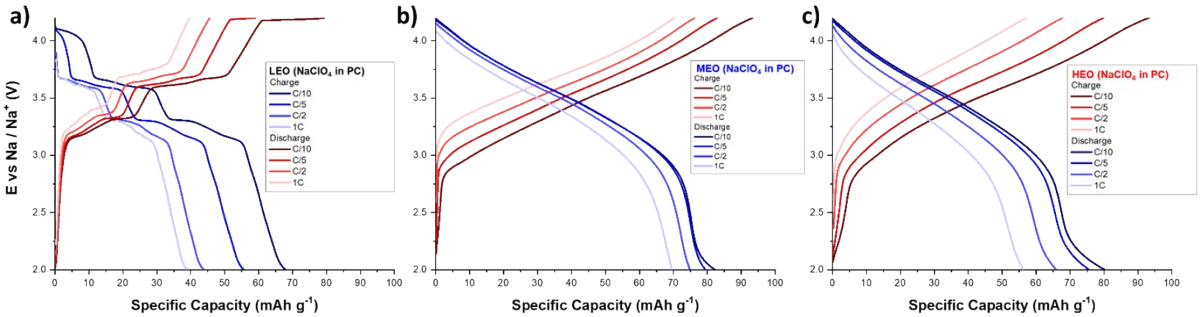


Figure S5*. Representative voltage vs. specific capacity profiles recorded at different C-rates upon galvanostatic charge/discharge cycling of Na metal cells based on* ***a)*** *LEO,* ***b)*** *MEO, and* ***c)*** *HEO with standard electrolyte ($NaClO_4$ 1M in PC), within the voltage range of 2.0–4.2 V vs Na^+/Na.*

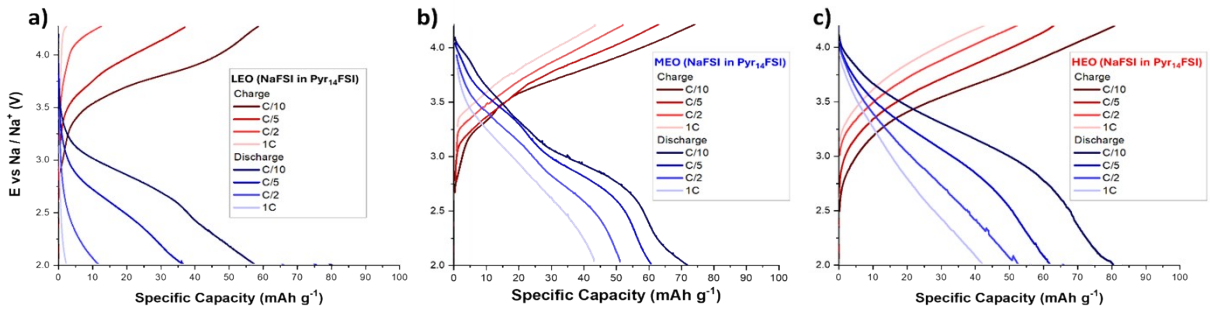


Figure S6. *Representative voltage vs. specific capacity profiles recorded at different C-rates upon galvanostatic charge/discharge cycling of Na metal cells based on* ***a)*** *LEO,* ***b)*** *MEO, and* ***c)*** *HEO with standard electrolyte (NaFSI in $Pyr_{14}FSI$ 1:4), within the voltage range of 2.0–4.2 V vs Na^+/Na.*

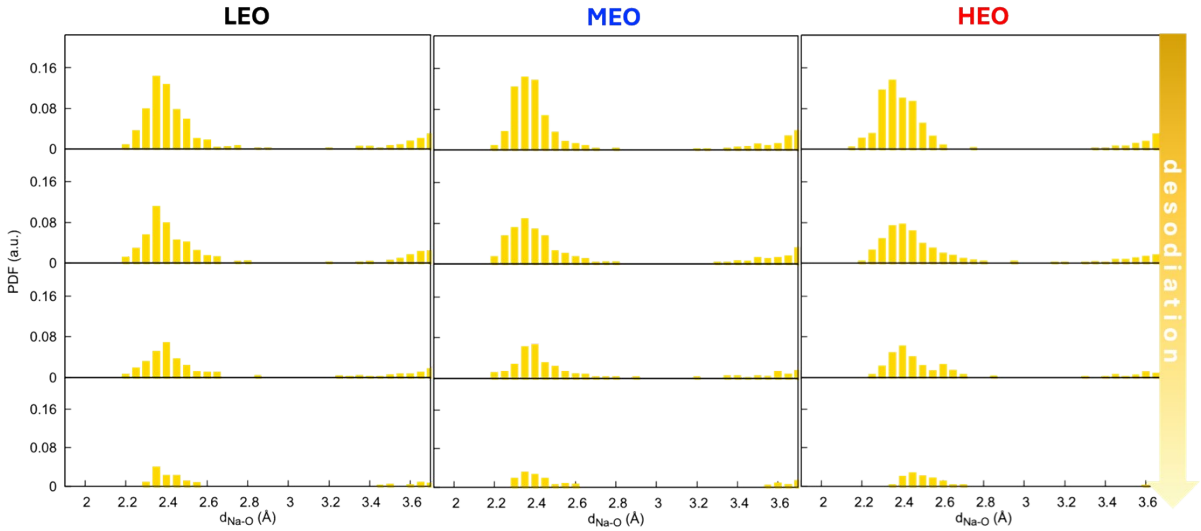
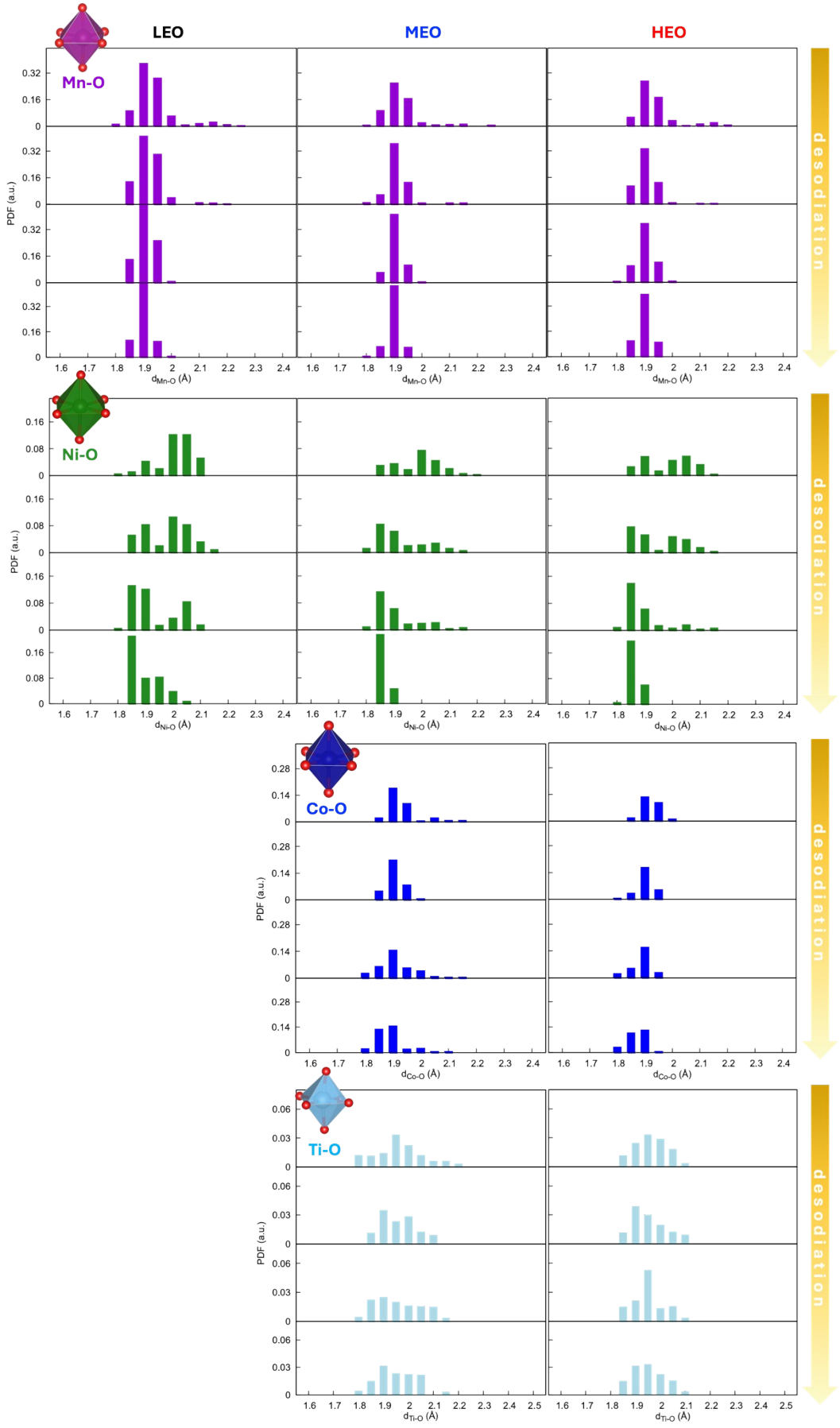


Figure S7. *Pair distribution function of Na-O distances computed for the PBE+U-D3BJ minimum-energy structures of LEO, MEO and HEO at different sodiation stages.*


LEO
MEO
HEO
Mn-O
Ni-O
Co-O
Ti-O
PDF (a.u.)
d_Mn-O (Å)
d_Ni-O (Å)
d_Co-O (Å)
d_Ti-O (Å)
desodiation

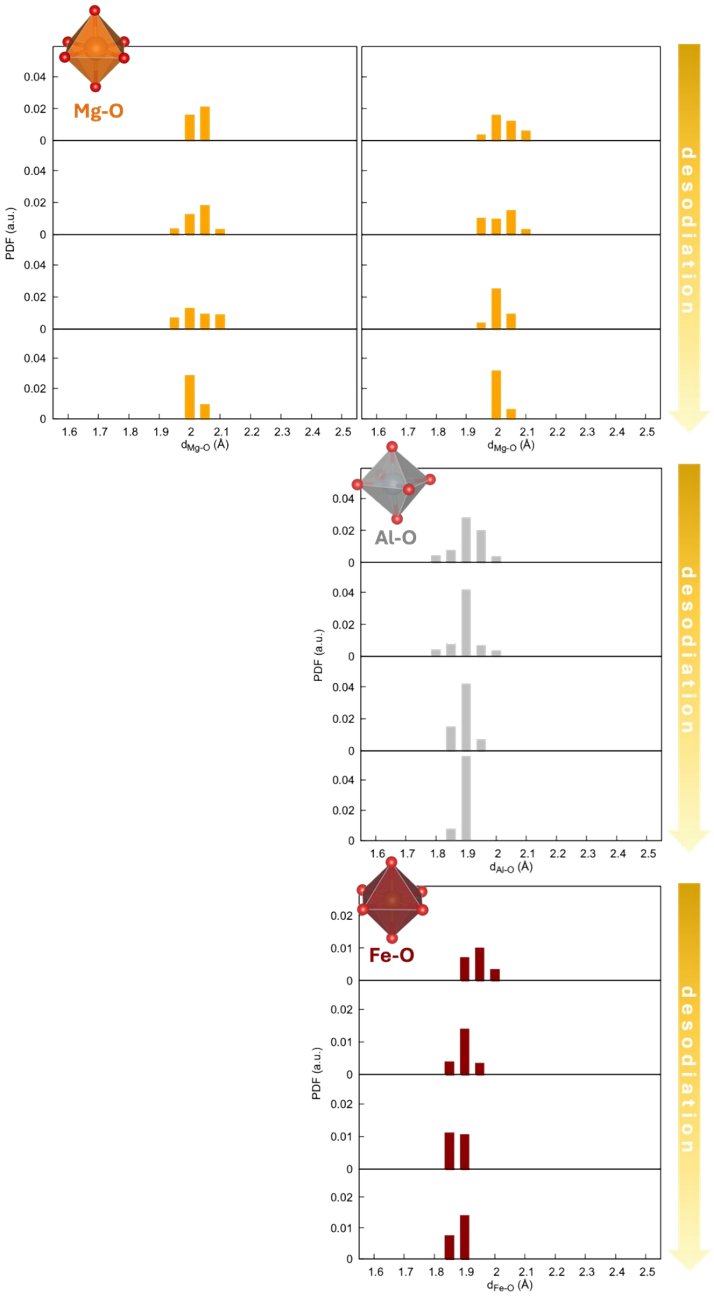


Figure S8. *Pair distribution function of M-O distances computed for the PBE+U-D3BJ minimum-energy structures of LEO, MEO and HEO at different sodiation stages.*