Insights into the Structure of Aluminum-Doped Manganese Dioxides for Direct Lithium Extraction: Modeling and Sorption Mechanism

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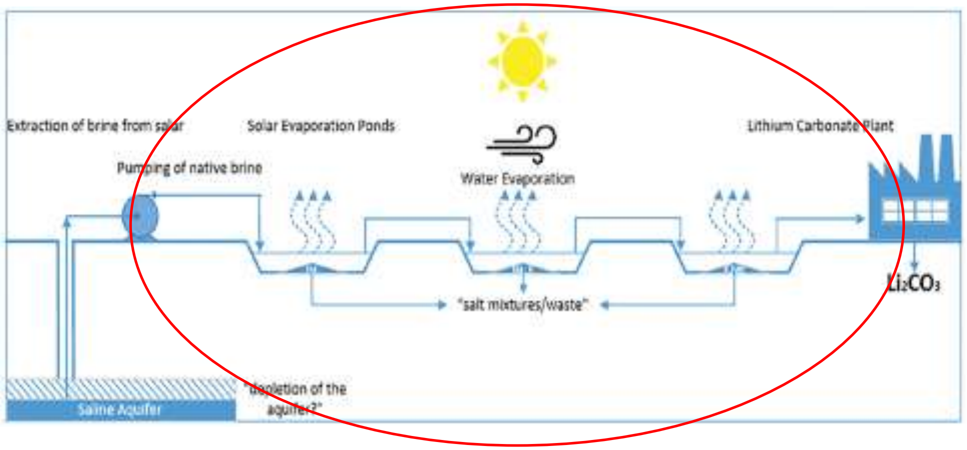
State of the Art –Direct Li Extraction

Conventional solar evaporation



- **Time-consuming,**
- **Land-intensive,**
- **Water-intensive,**
- **Weather-dependent**

Direct Lithium extraction (DLE) technology:

Lithium ions would be extracted selectively from a brine while all other salts would remain in the solution

- ✓ Highly efficient Li recovery
- ✓ Minimal environmental impacts
- ✓ A shorter time, lower in carbon footprint and less dependent on weather conditions

Desalination 577 (2024) 117406

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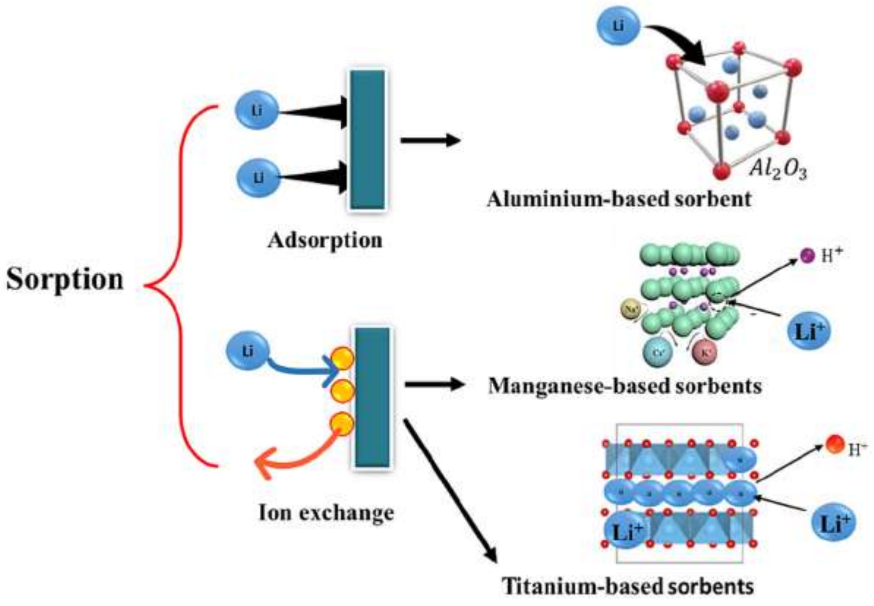
State of the Art –Direct Li Extraction

- Adsorption
- Ion exchange
- Solvent extraction
- Membrane
- Electrochemical



- - High selectivity
- - High separation efficiency
- - Low initial investment
- - High theoretical lithium-uptake
- capacity
- - Relatively low energy usage

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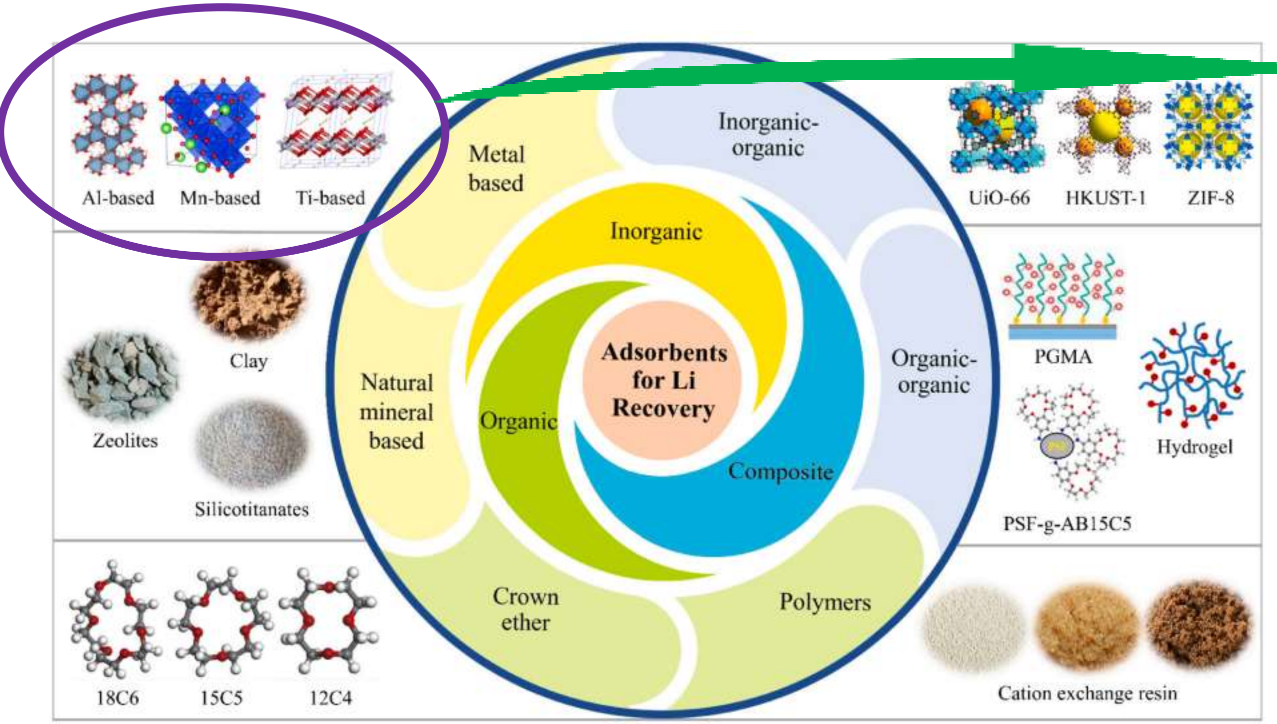
State of the Art

Most favourite materials for Li extraction



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Comparison of three types of metal-based adsorbents.

Performance	Al-based	Mn-based	Ti-based
Li Adsorption Capacity	★☆☆	★★☆	★★★
Li Selectivity	★☆☆	★★★	★★☆
Technology Maturity	★★★	★★☆	★☆☆
Stability and Regeneration Ability	★★★	★☆☆	★★☆
Facile Operation Condition	★★★	★☆☆	★★☆
Environmental Safety	★★★	★☆☆	★★☆
Low Preparation Cost	★★★	★☆☆	★★☆

Mn-based and Ti-based adsorbents are the most selective materials for Li extraction

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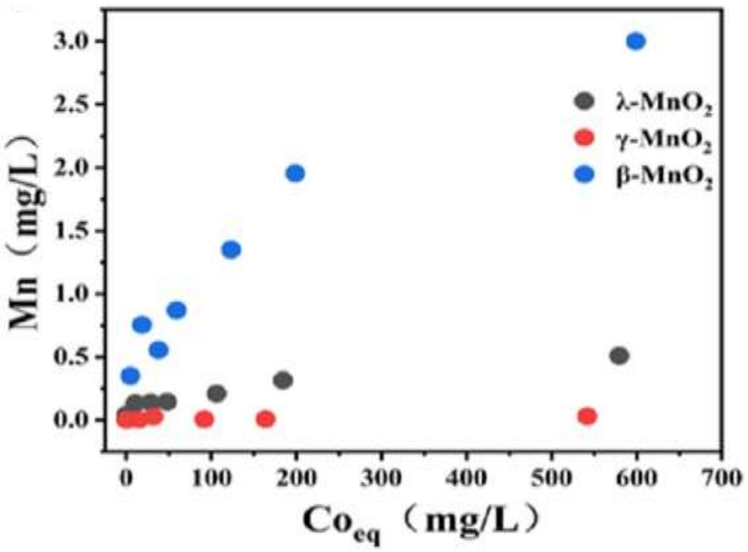
State of the Art-Problems to be solved

The dissolution of manganese from Mn oxide-based sorbents is inevitable and leads to a significant reduction in the amount of Li uptake.



J. Hazard. Mater. 425(2022)127957

The dissolution would directly affect the cycle life of lithium-ion sieves, and their capacities need to be enhanced.

Mn oxide-based sorbents as most favourite materials need optimization and further development

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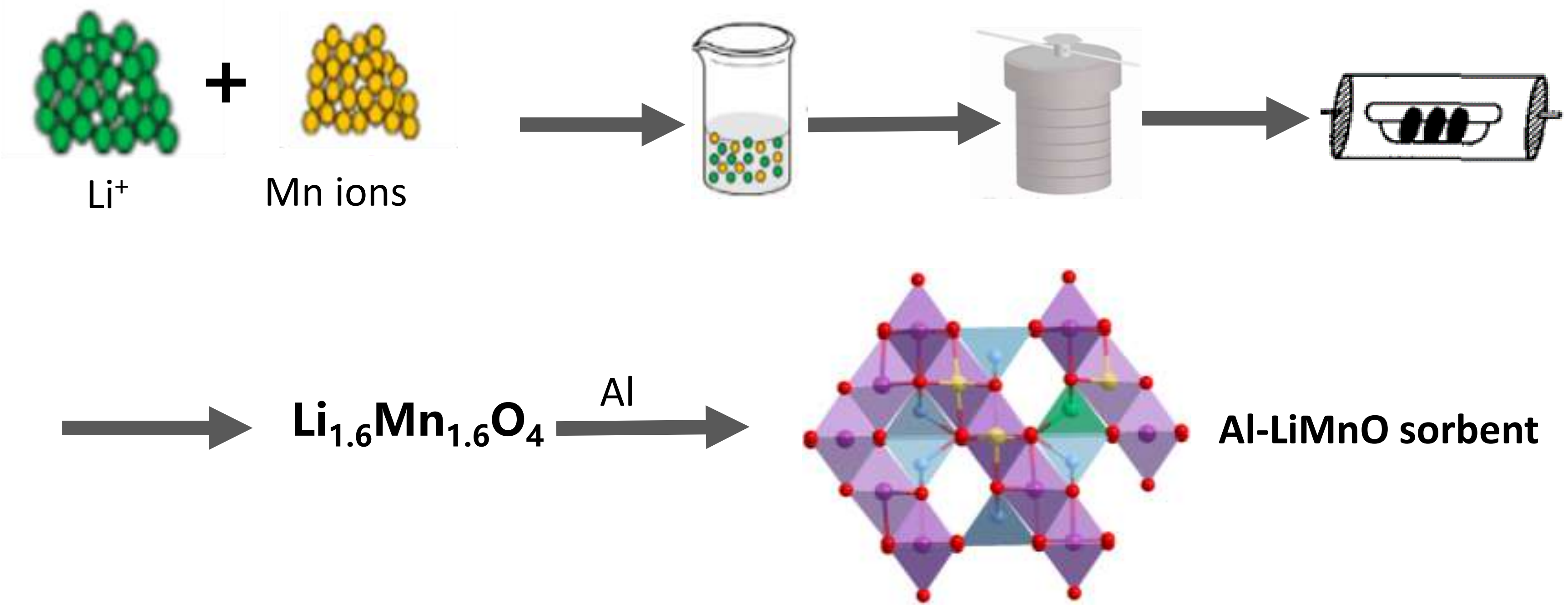
Synthesis and characterizations



Li^+ + Mn ions

$Li_{1.6}Mn_{1.6}O_4$ $\xrightarrow{Al}$ **Al-LiMnO sorbent**

Hydrothermal Method and Solid-State Calcination:

- Simple and easy to operate, allowing for uniform mixing of materials.
- The prepared materials have controllable morphology and size, good crystallinity, and high purity.

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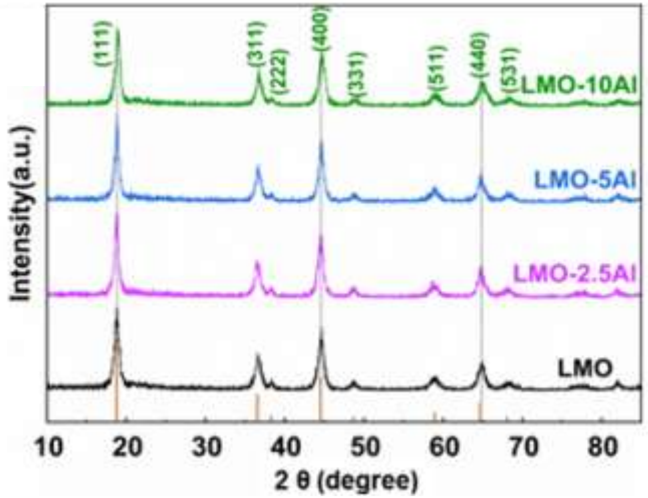
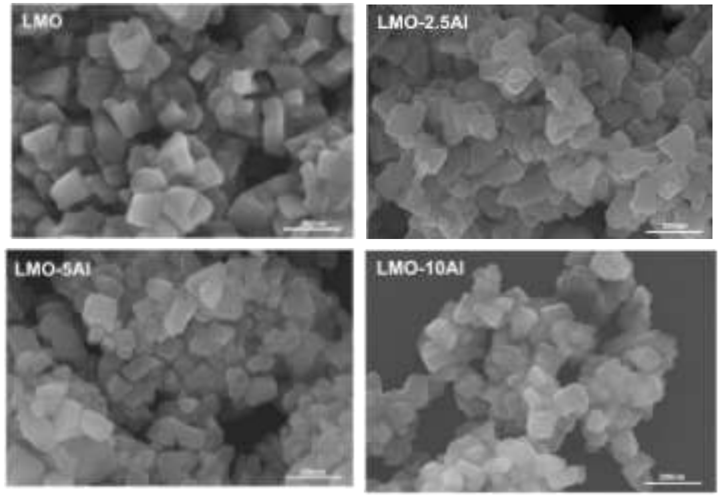
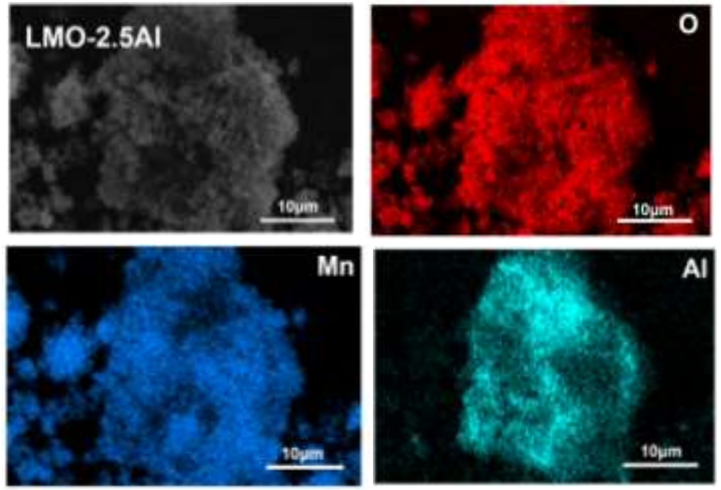
Synthesis and characterizations







$Li_{1.6}Mn_{1.6}O_4$ (LMO)
LMO-2.5Al (2.5% molar ratio Al/Mn)
LMO-5Al (5% molar ratio Al/Mn)
LMO-10Al (10% molar ratio Al/Mn)

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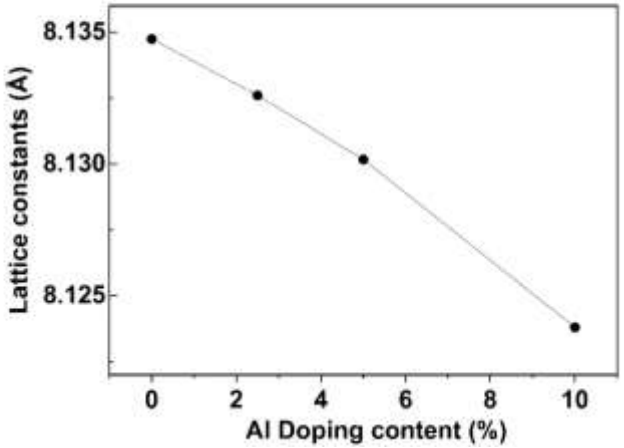
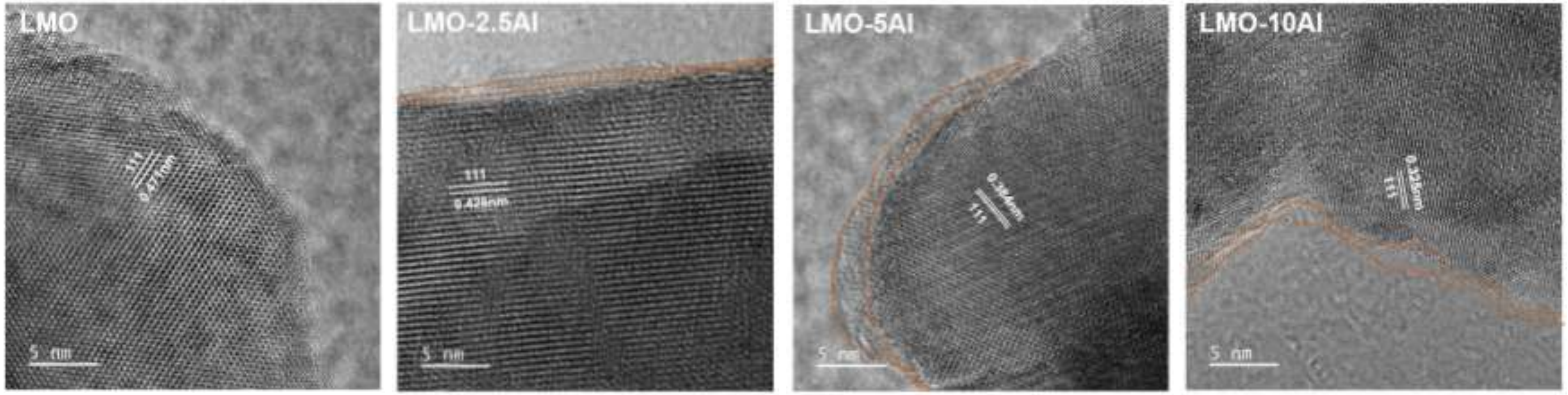
Synthesis and characterizations





As the amount of Al doping increases, the (111) crystal plane spacing decreases. This is because Al^{3+} partially replaces Mn, with the ionic radius of Al^{3+} ($r(Al^{3+})$ = 0.61 Å) being smaller than that of Mn^{4+} ($r(Mn^{4+})$ = 0.62 Å) and Mn^{3+} ($r(Mn^{3+})$ = 0.66 Å), corresponding to the lattice constants observed in the XRD analysis.

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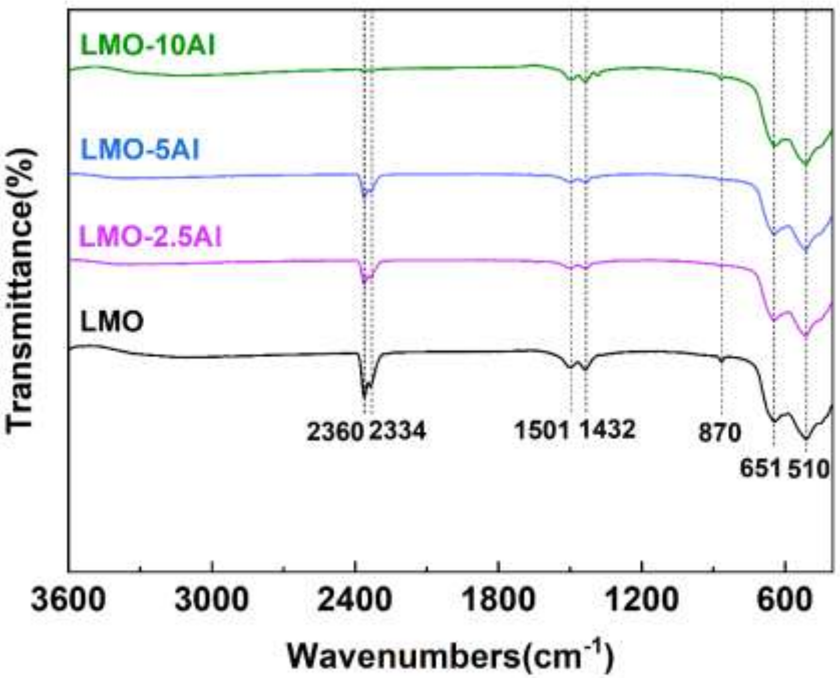
Synthesis and characterizations



cm^{-1}	
614-585	$[MnO_6]$ Mn-O
1123-1093	Li-O
1641-1632	-OH
3511-3476 cm^{-1}、3459-3408 cm^{-1}	H_2O

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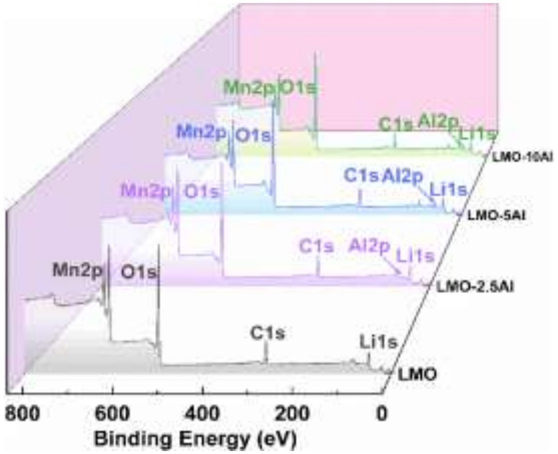
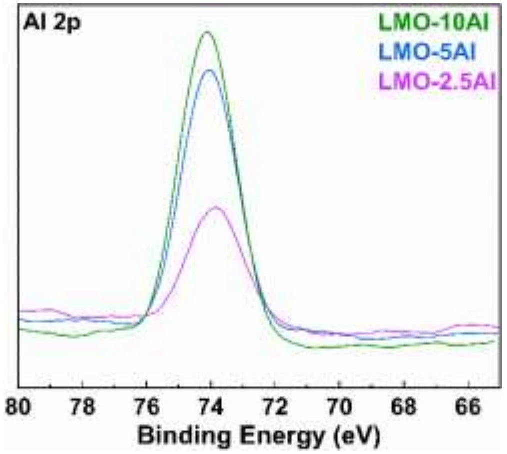
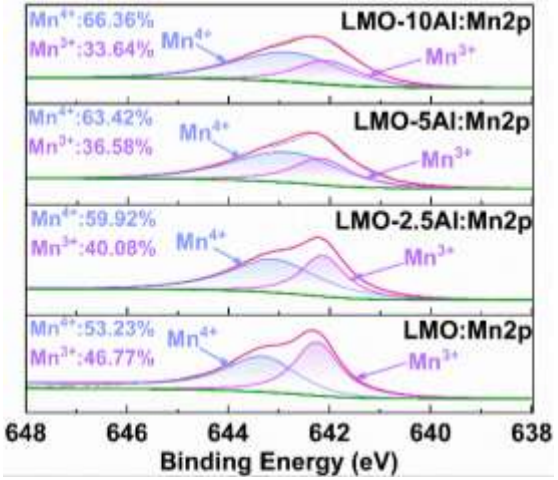
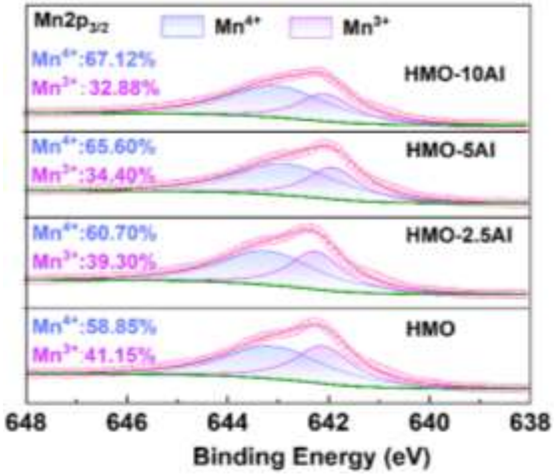
Synthesis and characterizations









- LMO: Mn^{4+}/Mn^{3+} = 1.14
- LMO-2.5Al : Mn^{4+}/Mn^{3+} = 1.49
- LMO-5Al : Mn^{4+}/Mn^{3+} = 1.78
- LMO-10Al : Mn^{4+}/Mn^{3+} = 1.81

- At the Al 2p peak: as the amount of Al doping increases, the corresponding peak (72-75 ev) intensity increases.

- HMO: Mn^{4+}/Mn^{3+} = 1.43
- HMO-2.5Al : Mn^{4+}/Mn^{3+} = 1.54
- HMO-5Al : Mn^{4+}/Mn^{3+} = 1.91
- HMO-10Al : Mn^{4+}/Mn^{3+} = 2.04

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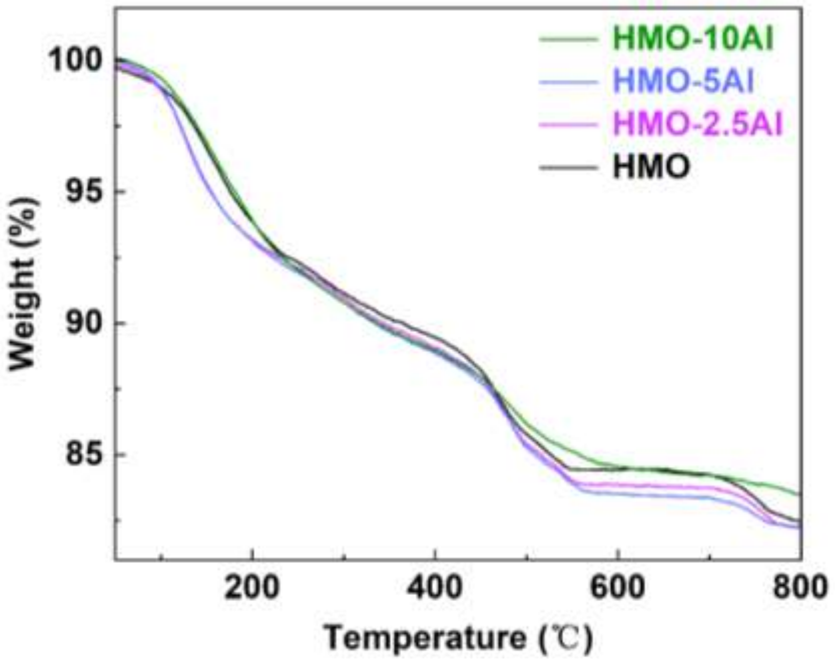
Synthesis and characterizations



The calculated chemical formula is shown in the table

Samples	Chemical formula
HMO	$Li_{0.035}H_{1.563}(Mn(III)_{0.412}Mn(IV)_{0.5885})_{1.652}\square_{0.474}O_{4.}0.23H_2O$
HMO-2.5Al	$Li_{0.010}H_{1.588}Al_{0.01}(Mn(III)_{0.393}Mn(IV)_{0.607})_{1.494}\square_{0.983}O_{4.}0.22H_2O$
HMO-5Al	$Li_{0.012}H_{1.588}Al_{0.052}(Mn(III)_{0.344}Mn(IV)_{0.656})_{1.534}\square_{0.636}O_{4.}0.22H2O$
HMO-10Al	$Li_{0.002}H_{1.600}Al_{0.087}(Mn(III)_{0.329}Mn(IV)_{0.671})_{1.436}\square_{0.865}O_{4.}0.23H2O$

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Batch experiments and modeling development

Batch experiments

- **Titration, pH adsorption, adsorption isotherm, Cyclic stability and coexisting ions experiments were conducted.**

Modeling development

- **Combining the geochemical software PHREEQC with the Python programming language.**
- **Two types of adsorption sites assumed exist on the surface of manganese-based lithium ion sieve powders: strong adsorption sites (≡S^{S}OH) and weak adsorption sites (≡SWOH).**
- **The existence of at least two types of physical sorption sites: planar and edge surface sites (S) and vacancies (W) within the structural framework.**

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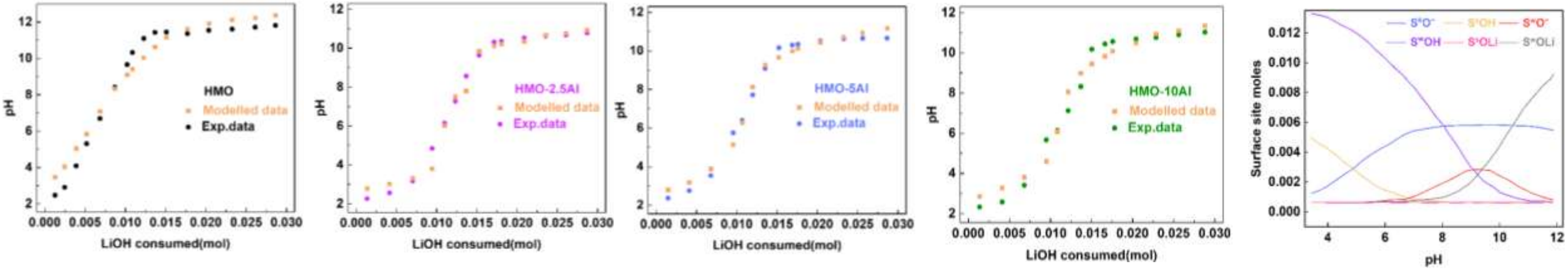
Batch experiments and modeling development

pH titration and modeling results of Al-$Li_{1.6}Mn_{1.6}O_4$ sorbents (LMO, LMO-2.5Al, LMO-5Al and LMO-10Al)



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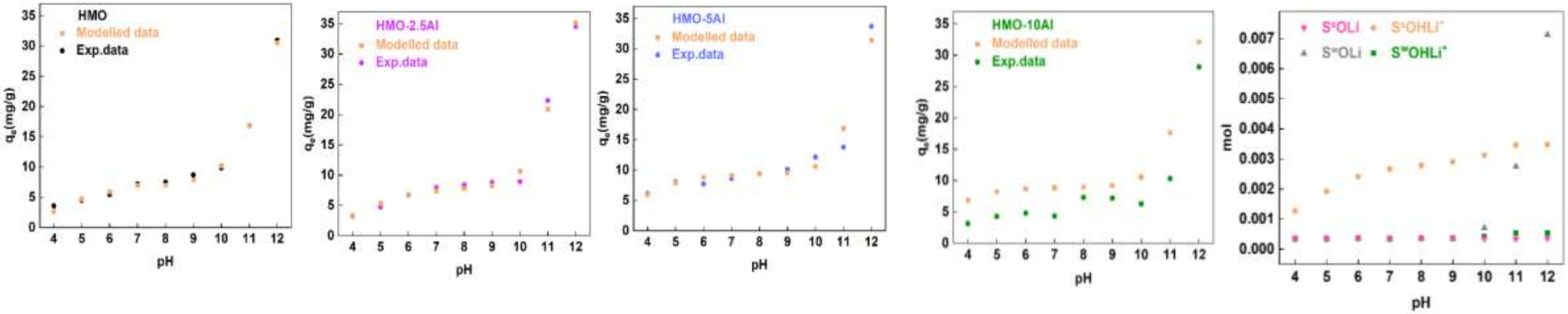
Batch experiments and modeling development

The effect of pH on the sorption capacity and their modeling results of sorbents (LMO, LMO-2.5Al, LMO-5Al and LMO-10Al)



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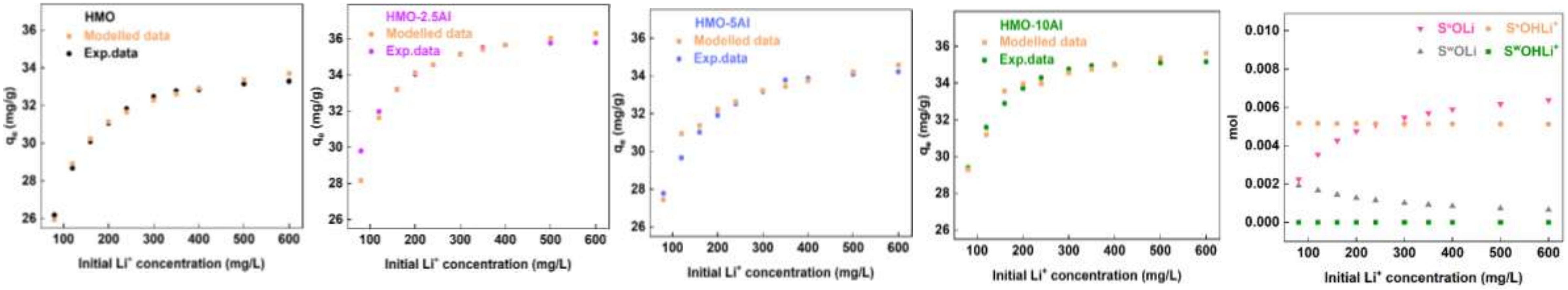
Batch experiments and modeling development

The isotherm sorption and their modeling results of sorbents （LMO, LMO-2.5Al, LMO-5Al and LMO-10Al)



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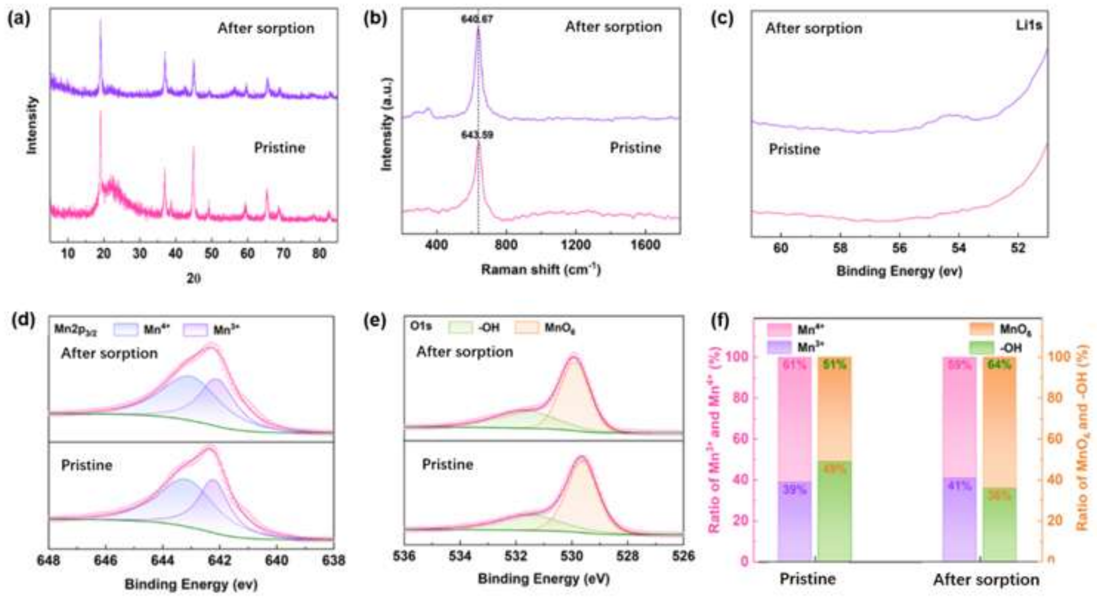
Batch experiments and modeling development

Sorption Mechanism study



Surface ion-exchange reaction

Surface complexation reaction

Sorption stage I (pH 12)

$\mathrm{Li^+ + {\equiv}S^wOH_2^+ = {\equiv}S^wOHLi^+ + H^+}$

$\mathrm{Li^+ + {\equiv}SSOH_2^+ = {\equiv}SSOHLi^+ + H^+}$

(Surface)

Sorption stage II (pH 12)

$\mathrm{{\equiv}S^WOH = {\equiv}S^WO^- + H^+}$

$\mathrm{Li^+ + {\equiv}SwO^- = {\equiv}SwOLi}$

(□ Vacancy)

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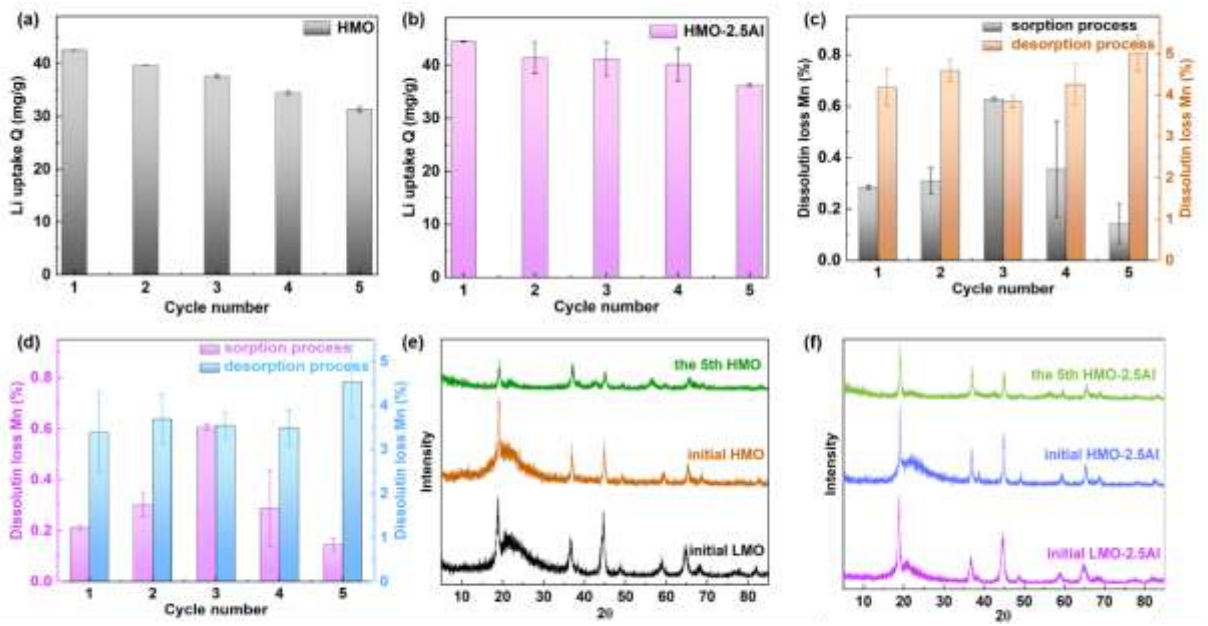
Cyclic stability test

- **Cyclic stability performance**



After five adsorption-desorption cycles:

- **the adsorption capacities of HMO-2.5Al slightly decreased to 36.23 mg/g**
- **The manganese dissolution loss rates of HMO-2.5Al increased to 4.53%.**

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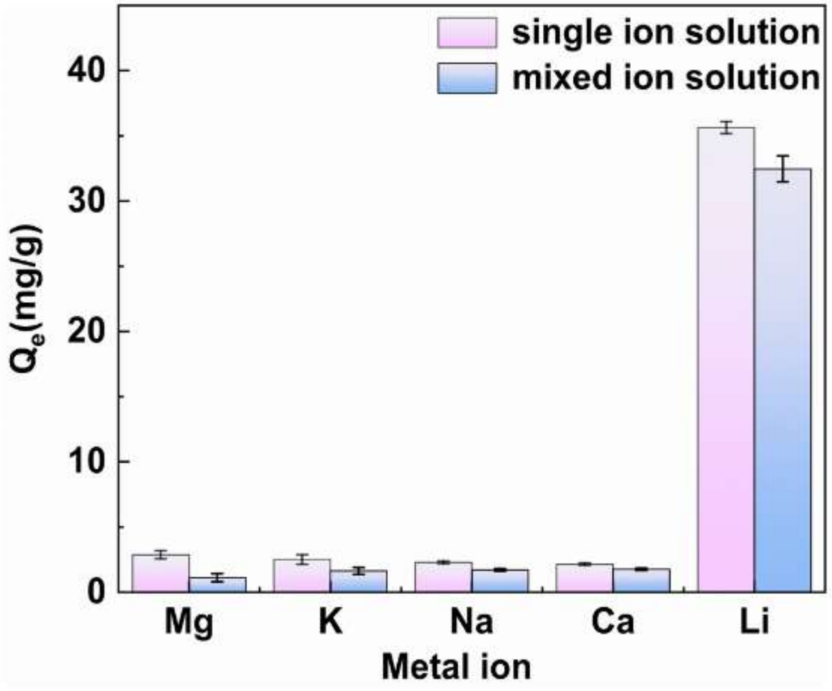
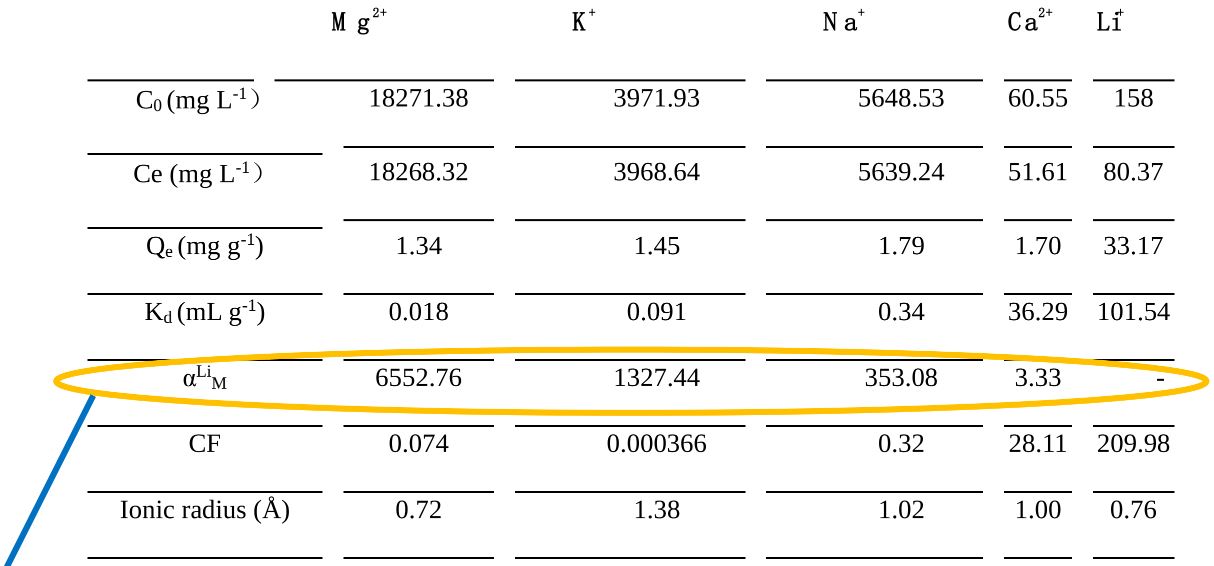
Effect of coexisting ions

Simulated salt lake brine sorption test





	Mg^{2+}	K^{+}	Na^{+}	Ca^{2+}	Li^{+}
C_0 (mg L^{-1})	18271.38	3971.93	5648.53	60.55	158
Ce (mg L^{-1})	18268.32	3968.64	5639.24	51.61	80.37
Q_e (mg g^{-1})	1.34	1.45	1.79	1.70	33.17
K_d (mL g^{-1})	0.018	0.091	0.34	36.29	101.54
α^{Li}_{M}	6552.76	1327.44	353.08	3.33	-
CF	0.074	0.000366	0.32	28.11	209.98
Ionic radius (Å)	0.72	1.38	1.02	1.00	0.76

High selectivity

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Effect of coexisting ions

Adsorbent	Solution	C_{Li}^{+}(mg L^{-1})	q_e (mg g^{-1})	References
$H_{1.6}Mn_{1.6}O_4$-Zr-2.4%	Salt Lake	150	25.96	Separation and Purification Technology, 303 (2022) 121933
$Li_{1.6}Mg_xMn_{1.6-x}O_4$	LiOH	156	35.6	Hydrometallurgy, 209 (2022) 105772.
HMO-Al-5%	LiCl	167	29.9	Separation and Purification Technology, 264 (2021) 118433.
$LiMn_{2-x}Fe_xO_4$	LiCl	200	34.8	Journal of Materials Research and Technology, 13 (2021) 228-240
$LiAl_xMn_{2-x}O_4$	LiOH	50	27.66	Microporous and Mesoporous Materials, 261 (2018) 29-34.
$Li_{1.6}Mn_{1.6}O_4$	Salt Lake	266	27.15	Hydrometallurgy, 110 (2011) 99-106.
$Li_{1.6}Mn_{1.6-x}Cr_xO_4$	Salt Lake	222	31.67	Bulletin of the Chemical Society of Japan, 92 (2019) 1205-1210.
HMO/Al_2O_3	Seawater	30	6.2	Industrial & Engineering Chemistry Research, 58 (2019) 8342-8348
$H_{1.6}Mn_{1.6}O_4$/PAN	LiCl/LiOH	35	10.3	Chemical Engineering Journal, 254 (2014) 73-81.
LMO-Na	LiCl	167	33.5	Separation and Purification Technology, 256 (2021) 117583
HMO	LiOH	150	42.60	This study
HMO-Al-2.5%	LiOH	150	44.49	This study

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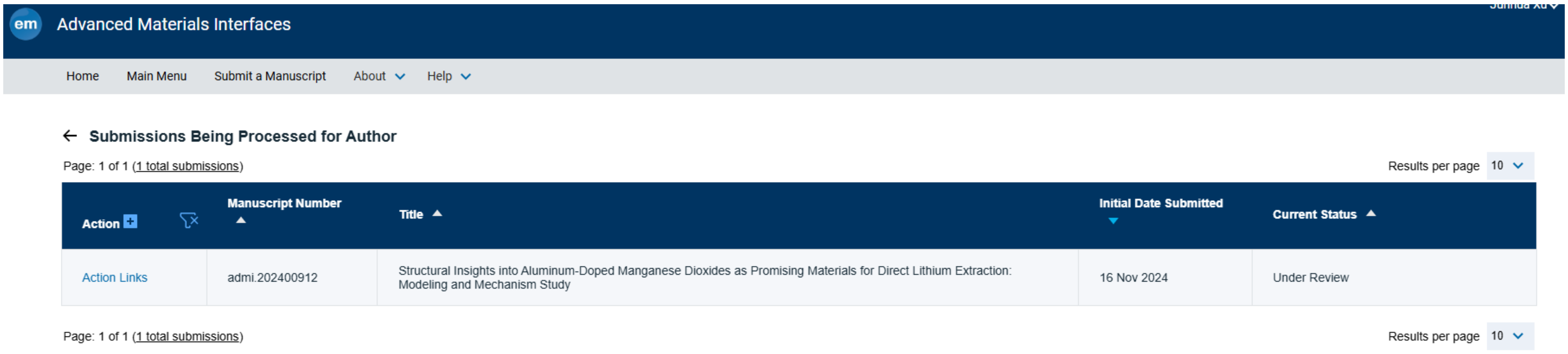
Manuscript submitted



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