Modeling intercalation chemistry with multi-redox reactions by sparse lattice models

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Introduction

Background

- Sustainable energy storage materials for electric vehicles (EVs) applications.
- Disordered rocksalt materials **(DRX)** can be composed of many earth-abundant transition metals (**TM**), in compositional formula of $Li_{1+x}TM_{1-x}O_{2-y}F_y$.
- The **multi-component** and **multi-redox** nature make computational modeling complex (high-dimensional parameter space).

Preliminaries

- **Cluster expansion** casts the energy from *ab-initio* calculation as a function of the occupancy of atoms on a set of predefined sites [1]:

$$E(\boldsymbol{\sigma}) = \sum_{\beta} m_\beta J_\beta \langle \Phi_{\boldsymbol{\alpha}\in\beta} \rangle_\beta + \frac{E_0}{\varepsilon_r},\ \Phi_{\boldsymbol{\alpha}} = \prod_{i=1}^{N} \phi_{\alpha_i}(\sigma_i). \quad (1)$$

- The approximated equilibrium voltage profile at T = 0 K:

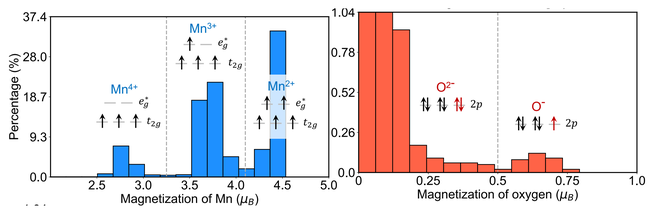
$$\bar{V}(x_1, x_2) \approx -\frac{E_{\mathrm{Li}_{x_1}\mathrm{TMO}_2} - E_{\mathrm{Li}_{x_2}\mathrm{TMO}_2} - (x_1 - x_2)E_{\mathrm{Li}}}{F(x_1 - x_2)}. \quad (2)$$

- Semigrand canonical Monte Carlo is used to sample the relation between Li concentration (x_{Li}) and the chemical potential μ_{Li} (voltage) at finite T:

$$V(\bar{x}) = -\frac{\mu_{\mathrm{Li}} - E_{\mathrm{Li}}}{e}, \quad f(E(\boldsymbol{\sigma}), \boldsymbol{\mu}) \propto \exp\left(-\frac{E(\boldsymbol{\sigma}) - \boldsymbol{\mu}\cdot\boldsymbol{x}N}{k_B T}\right) \quad (3)$$

Technique Highlights

(1) Charge differentiation by magnetic moments



- Transition metal redox: $\mu_{Mn^{3+}} \in [3.25\mu_B,\ 4.1\mu_B]$, $\mu_{Mn^{2+}} \in [4.1\mu_B,\ 5.0\mu_B]$
- Oxygen redox: $\mu_{O^{2-}} \in [0\mu_B,\ 0.5\mu_B]$, $\mu_{O^-} \in [0.5\mu_B,\ 1.0\mu_B]$

(2) Sparse regression model for lattice cluster expansion [2]

$$\min_{\boldsymbol{J}}\ \boldsymbol{J}^T\boldsymbol{\Pi}_S^T\boldsymbol{\Pi}_S\boldsymbol{J}^T - 2\boldsymbol{E}_{\mathrm{DFT}}^T\boldsymbol{\Pi}_S\boldsymbol{J} + \mu_0\sum_{c\in\boldsymbol{C}} z_{0,c} + \mu_2||\boldsymbol{J}||_2^2 \quad (4)$$

$$\begin{aligned} \boldsymbol{s.t.}\quad & Mz_{0,c} \geq J_c,\ \forall c \in \boldsymbol{C} \\ & Mz_{0,c} \geq -J_c,\ \forall c \in \boldsymbol{C} \\ & z_{0,b} \leq z_{0,a},\ \forall a \subset b,\ \{a,b\} \in \boldsymbol{C} \\ & z_{0,c} \in \{0,1\},\ \forall c \in \boldsymbol{C}, \end{aligned}$$

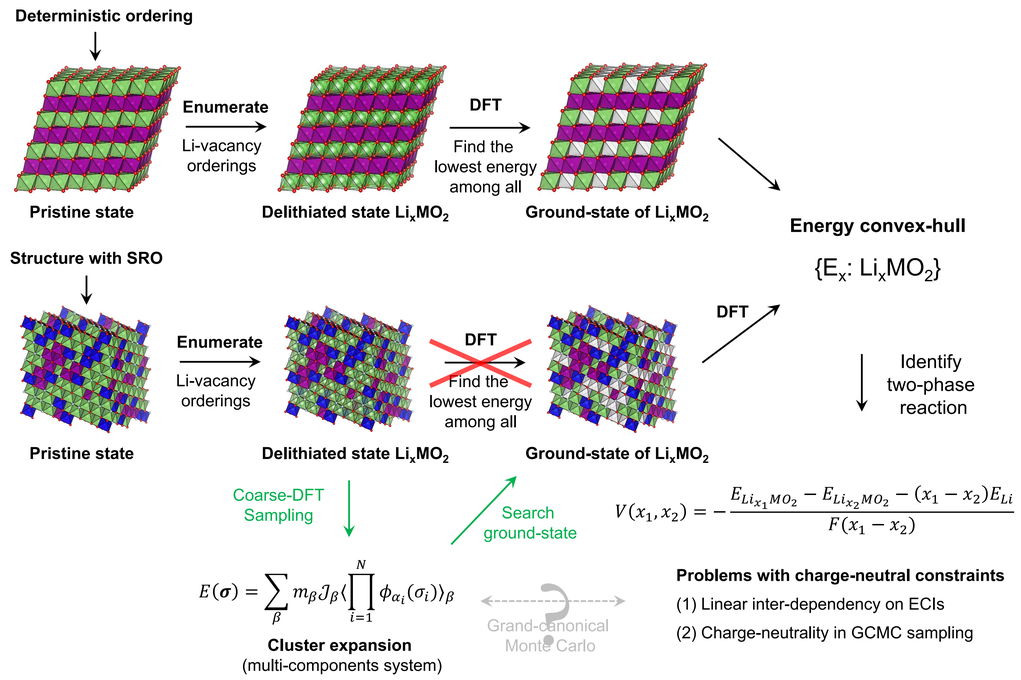
(3) Charge-balanced sampling in semigrand canonical MC [3]

Allowed
$$\begin{cases} Li^+ + Mn^{2+} & \leftrightarrow\ Mn^{3+} + \mathrm{Vac} \\ Li^+ + Mn^{3+} & \leftrightarrow\ Mn^{4+} + \mathrm{Vac} \\ Li^+ + O^{2-} & \leftrightarrow\ O^- + \mathrm{Vac}. \end{cases}$$

Forbidden $Li^+ \leftrightarrow Mn^{2/3/4+}$ || $Mn^{2/3/4+} \leftrightarrow Nb^{5+}$ || $O^{2-/-} \leftrightarrow F^-$

[1]L. Barroso-Luque et al., Physical Review B **106**, 144202 (2022).
[2]P. Zhong et al., Physical Review B **106**, 024203 (2022).
[3]F. Xie et al., Computational Materials Science **218**, 112000 (2023).
[4]L. Huang et al., Advanced Energy Materials **13**, 2202345 (2023).
[5]P. Zhong, F. Xie, and G. Ceder, Bulletin of the APS (2023).
[6]B. Deng, P. Zhong, and G. Ceder, Bulletin of the APS (2023).

Challenges of voltage profile modeling in DRX systems



$$V(x_1, x_2) = -\frac{E_{Li_{x_1}MO_2} - E_{Li_{x_2}MO_2} - (x_1 - x_2)E_{Li}}{F(x_1 - x_2)}$$

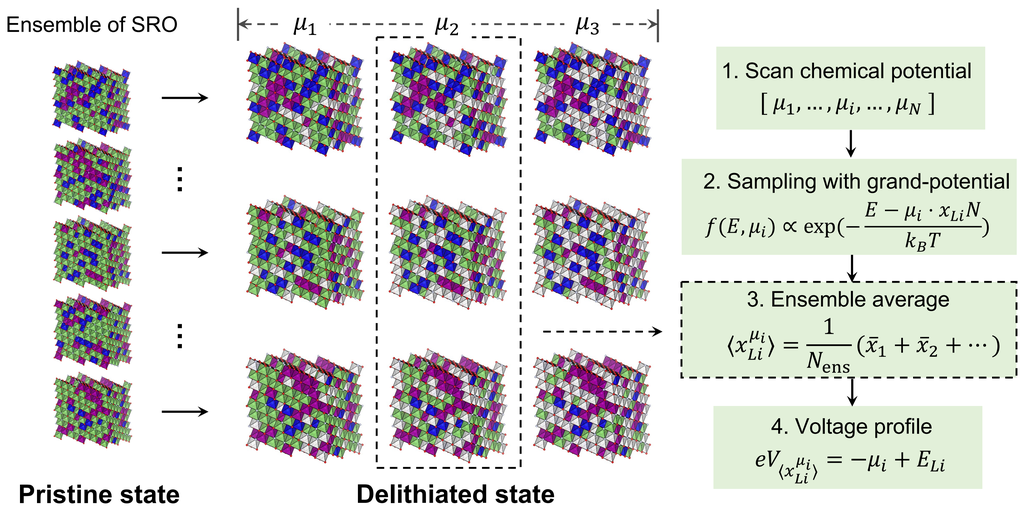
$$E(\boldsymbol{\sigma}) = \sum_{\beta} m_\beta \mathcal{J}_\beta \langle \prod_{i=1}^{N} \phi_{\alpha_i}(\sigma_i) \rangle_\beta$$

Problems with charge-neutral constraints

(1) Linear inter-dependency on ECIs

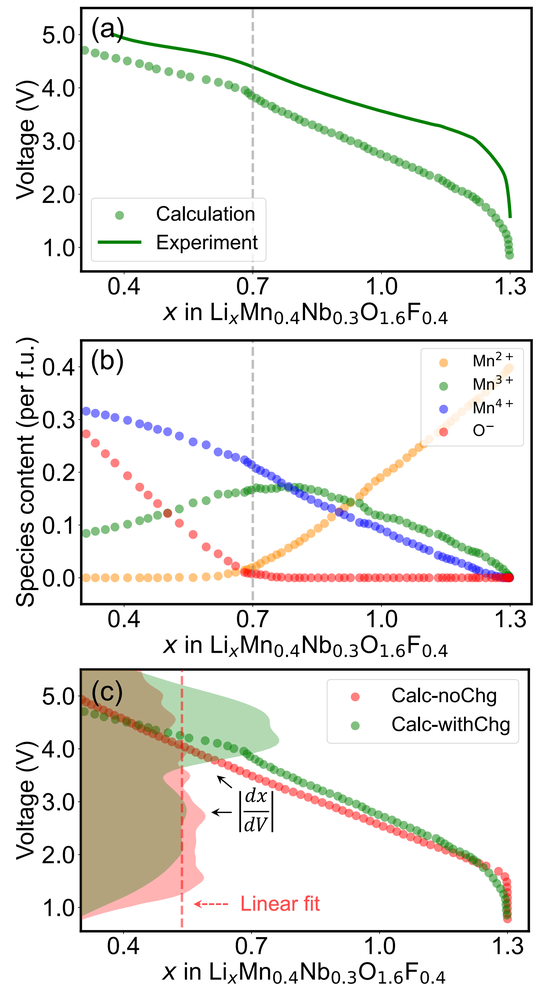
(2) Charge-neutrality in GCMC sampling

An illustration of charge-balanced semigrand canonical Monte Carlo for DRX systems



We combined the sparse lattice cluster expansion, charge-balanced MC sampling, and ensemble-average method to generate the equilibrium voltage profile of DRX [4, 5].

Numerical Simulations



Conclusion & Outlook

- DRX cathode design benefits from the abundance of **redox-active** transition metals such as Cr, V, Mn, Fe, etc. **Curse of dimensionality (CoD)** is a major simulation obstacle due to the complex multi-component and multi-redox nature of DRX materials
- **Proposed workflow for DRX voltage profiles:** **(1)** Training set: different fully lithiated structures + different Li/vacancy orderings; **(2)** meta-GGA functional (r^2SCAN) for DFT calculations; **(3)** construct a **charge-decorated** CE Hamiltonian using the sparse regression; and **(4)** run semigrand canonical MC in an ensemble of SRO structures under **charge balances**.
- Modern **machine-learning interatomic potential (MLIP)** methods provide new opportunities to accelerate the training structure generation process, especially the **charge-informed MLIP** enables the detailed study of redox-related phenomena in cathode materials [6].