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Machine learning assisted screening of materials for Li-ion batteries

Razvoj materijala za litijum-jonske baterije korišćenjem mašinskog učenja

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Abstract

The development of novel materials is seen as the key approach to improvements in the performance of Li-ion batteries. Recently, conversion-type electrodes have been demonstrated to improve battery capacity and energy density. Metal hydrides are considered promising anode materials, while some hydride materials are also considered solid ionic conductors. In this research, we rely on the machine learning approach to predict the properties of novel anode materials depending on hydride conversion reactions. We limit our search to Mg-containing intermetallic compounds and screen a vast database of optimized crystal structures obtained using density functional theory calculations. The composition and crystal structure of selected metals/intermetallics are input for a graph neural network-based machine learning model to predict hydride formation enthalpy and equilibrium electrode potential vs. Li^+/Li^0. Among 245 intermetallic compounds found to be satisfactory as anode materials, we particularly discuss La-Mg-X intermetallics. The work demonstrates the advantages of combining artificial intelligence tools and theoretical approaches with experimental results for property prediction and fast screening of vast combinatorial space.

Keywords: *Li-ion batteries; anodes; machine learning; metal hydride; Mg*

Izvod

Brojna istraživanja usmerena su na razvoj novih materijala kao ključnog pristupa u poboljšanju performansi litijum-jonskih baterija. Poslednjih godina posebno se ispituju konverzione elektrode koje omogućavaju veće kapacitete i gustine energija. Posebno, metalni hidridi se ispituju kao pogodni materijali za anode konverzionog tipa, dok se takođe neki hidridi ispituju i kao pogodni jonski provodnici. U ovom radu koristimo modele mašinskog učenja za predviđanje osobina novih anodnih materijala, oslanjajući se na reakcije konverzije hidrida. Pretraga novih intermetalnih jedinjenja ograničana je na one koji sadrže magnezijum, a kao izvor podataka korišćene su dostupne baze kristalnih struktura oprimizovanih proračunima zasnovanim na teoriji funkcionala gustine. Sastav i kristalna struktura odabranih metala/intermetalnih jedinjenja korišćeni su kao ulazni podaci za model mašinskog učenja zasnovan na graf neuronskim mrežama. Na taj način predviđene su entalpije formiranja hidrida i ravnotežni elektrodni potencijali u odnosu na Li^+/Li^0. Od 245 intermetalnih jedinjenja koja zadovoljavaju uslov za anodni materijal izdvojena su i diskutovana ternarna jedinjenja La-Mg-X. Ovaj rad pokazuje prednost kombinovanja alata veštačke inteligencije i teorijskih pristupa sa eksperimentalnim radom u cilju predviđanja osobina novih materijala i brze pretrage velikog prostora mogućih intermetalnih jedinjenja.

Ključne reči: *litijum-jonske baterije; anode; mašinsko učenje; metalni hidridi; magnezijum*

Introduction

The development of innovative electrode materials [1] and novel solid-state electrolytes [2] is seen as a route toward the improvement of Li-ion batteries (LIBs). The relatively low theoretical capacities and the problem of capacity fading in the active materials of classical intercalation reactions led to the consideration of novel anode electrode materials, including various conversion materials. Metal hydrides have been demonstrated to have a high theoretical capacity and energy density [2,3]. In addition, some metal hydrides are investigated as solid-state electrolytes [4].
The expansion of machine learning (ML) and artificial intelligence (AI) approaches in the last decade led to a new scientific paradigm in material discovery and optimization [5]. The data-centric approach in materials science and the development of accurate ML models enable the prediction of various material properties. In particular, hydride materials' thermodynamic characteristics, hydrogen storage properties [6,7,8], and solid compounds' ionic conductivity [9] are addressed.
Motivated by the importance of LIBs and opportunities offered by in-silico material design, we provide machine learning-guided exploration of potential conversion-type anode materials for LIBs.

Methodology

Data acquisition and machine learning approach

To consider hydride-forming intermetallic compounds which can be used as conversion-type electrodes in LIBs, we examined the Material Project (MP) database [10] containing a large number of crystal structures optimized using density functional theory (DFT). We limit our search to Mg-containing intermetallic compounds shown to be stable in DFT calculations. The latter is ensured by posing a constraint of intermetallic stability in DFT calculations (energy above convex Hull equals 0).
Hydride formation enthalpy and equilibrium potential of metal hydride conversion electrode for LIBs are obtained using MetalHydEnth[11], a graph neural network model. The model considers intermetallic compounds' chemical composition and crystal structure by transforming structural features into an index-type graph. A graph node corresponds to the vector of atomic numbers of constituent atoms. Edges of the graph are constructed for atom pairs within 5Å of spatial distance. In addition, the global states placeholder is initialized to store information and as a portal to enter state variables (e.g., temperature). All state attributes (atom, bond, global) are interconnected by definition and updated simultaneously through message-passing MEGNet blocks. A 16-dimensional element embedding layer, obtained from the Mp-2019.4.1 model [12] trained on the data set containing 133,420 data from the Materials Project [10], is included as the chemical intuition layer in the transfer learning approach.
The model predicts the heat of hydride formation based on the crystal structure and atomic composition, with a mean absolute error (MAE) value of 9.1kJ/molH_2 and MAE of 5.5kJ/molH_2 for Mg-containing intermetallics [8]. Hydride formation enthalpy (ΔH_{hyd}) is obtained as ΔH_{hyd}= - the heat of hydride formation. Enthalpy change in the reaction of hydride formation (expressed in kJ/molH_2) is obtained for any input struct file. Importantly, representing the enthalpy of hydride formation reaction in kJ/molH_2 allows comparison of various metal hydrides regardless of the stoichiometry of their hydride formation reaction.

Theoretical background

In metal hydride Li-ion batteries, a conversion reaction between LiH and metal hydride (MH_x) occurs at the anode [3]. The overall reaction and the corresponding change in the Gibbs free energy at T=25˚C are presented in equations (1) and (2).

$$MH_x + xLi^+ + xe^- \leftrightarrow M^0 + xLiH \quad (1)$$

$$\Delta_r G^\circ_{298} = x\Delta_f G^\circ_{298}(LiH) - \Delta_f G^\circ_{298}(MH_x) = -xEF \quad (2)$$

Changes in Gibbs free energy during metal hydride formation for all metal-hydrogen systems are reasonably approximated by the entropy change of 130 J/K mol H_2. Therefore the enthalpy change remains the variable that determines the behavior of various metal hydrides. Taking the experimental value for the difference in Gibbs free energy in the formation of LiH and enthalpy of hydride formation in intermetallic compound predicted by the machine learning model, we calculate the equilibrium potential versus Li^+/Li^0 following equation (3):

$$E^\circ_0 = \frac{\Delta_f G^\circ_{298}(LiH)}{F} - \frac{\Delta_f G^\circ_{298}(MH_x)}{xF} \quad (3)$$

Results and discussion

Mg-containing alloys are selected as promising candidates, given that MgH_2 conversion electrodes are already demonstrated and that availability and low cost of Mg make them promising for broad applications. The initial search on the Materials Project database gave over 19000 compounds containing Mg. Applying conditions regarding stability and composition listed in the methodology section, we obtain 437 Mg-containing intermetallics. For all of them, hydride formation enthalpy prediction is made using MetalHydEnth [11], and the equilibrium potential of conversion electrode versus Li^+/Li^0 (in the text also referred as potential or equilibrium potential) is calculated as explained in the chapter theoretical background. Figure 1 displays the predictions as the function of volume per atom in the intermetallic compound.

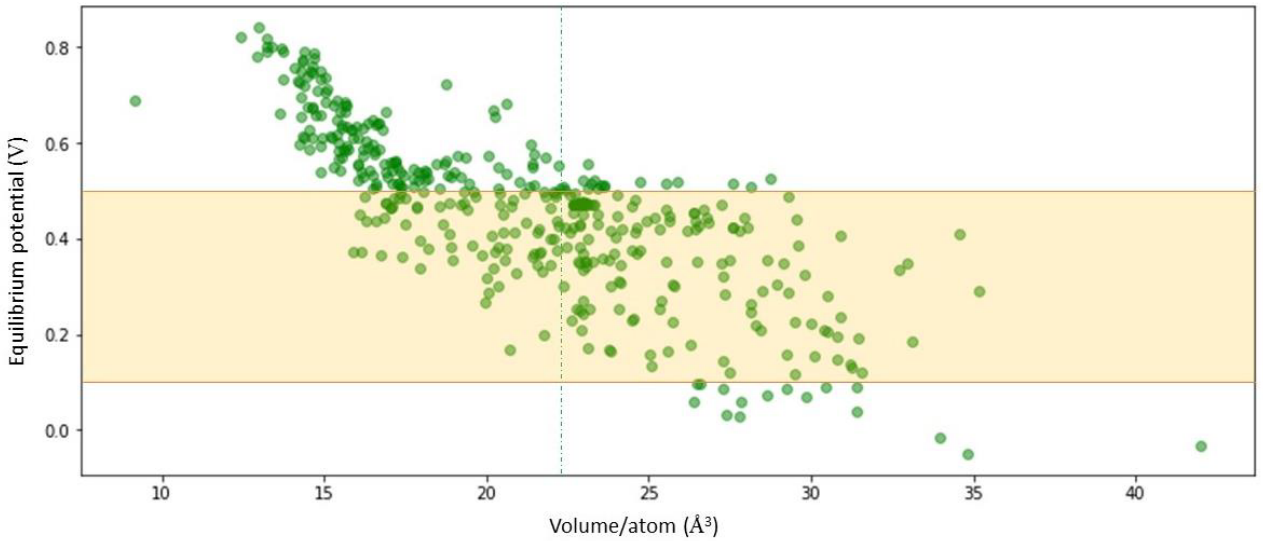

Figure 1. *Equilibrium potential of conversion-type metal hydride electrode vs. Li^+/Li^0 as a function of volume per atom in corresponding metal/intermetallic compound. The dashed vertical line shows the volume per atom in Mg metal, while the orange horizontal region marks desired 0.1-0.5V potential range.*

In the search for negative electrodes in Li-ion batteries, 0.1–0.5 V versus Li^+/Li^0 is taken as the safe potential range [3]. Of the 437 Mg-containing compounds, 245 have predicted potentials in this range, as marked in fig.1. We consider them further. Fig. 2 displays some properties of this subset.

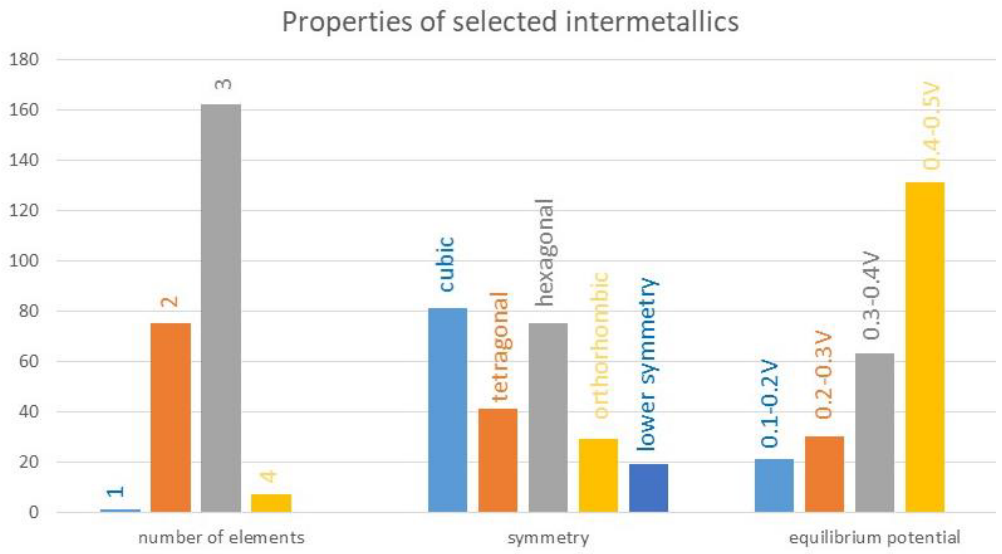

Figure 2. *Charts presenting selected properties (number of distinct elements, symmetry of the unit cell, and range of the predicted potentials) of 245 Mg-containing intermetallics selected as potential materials for conversion-type anodes in Li-ion batteries.*

As seen from the charts in fig.2, most selected intermetallics are ternary and binary. The predicted range of equilibrium potential is near the one for pure magnesium (0.56 V) (13) in many binary intermetallics of formula $Mg_{149}X$; these are omitted from the discussion, due to a slight variation in their enthalpy of hydride formation compared to MgH_2.

Table 1. Dominant elements among 245 intermetallics having 0.1-0.5 V equilibrium potential vs. Li^+/Li^0. Determined equilibrium potentials for binary intermetallics and potential range for ternary intermetallics are provided

Element	Binary compound	Potential (V)	No. ternary compounds	Potential range (V)
Ba	Ba_2Mg_{17} Ba_6Mg_{23}	0.43 0.28	11	0.19-0.35
Ca	/	/	11	0.12-0.41
Ce	$CeMg_3$	0.44	16	0.27-0.45
Gd	GdMg $GdMg_3$	0.42 0.49	11	0.41-0.47
La	LaMg $LaMg_3$	0.14 0.42	22	0.13-0.50
Sr	Sr_6Mg_{23}	0.36	10	0.12-0.35
Sc	MgSc $MgSc_2$	0.35 0.17	10	0.17-0.46
Nd	NdMg $NdMg_3$	0.29 0.46	27	0.21-0.49
Y	YMg YMg_3	0.12 0.43	19	0.14-0.42

A more detailed examination of ternary compounds is done. When alloyed with Mg, certain elements provide the most suitable intermetallics that are candidates for conversion electrodes. We identified Ba, Ca, Ce, La, Sr, Sc, and Nd as the most dominant elements in these compounds, which modulate Mg properties favorably for this application. These elements and the number of obtained ternary compounds containing them in addition to Mg are listed in Table 1.
In addition, we examine La-containing intermetallics, given that La compounds are well-established, stable hydride-forming materials. Fig.3 displays binary and ternary La-Mg containing intermetallics determined to have suitable potential vs. Li^+/Li^0 electrode, where each intermetallic is presented based on the crystal structure.

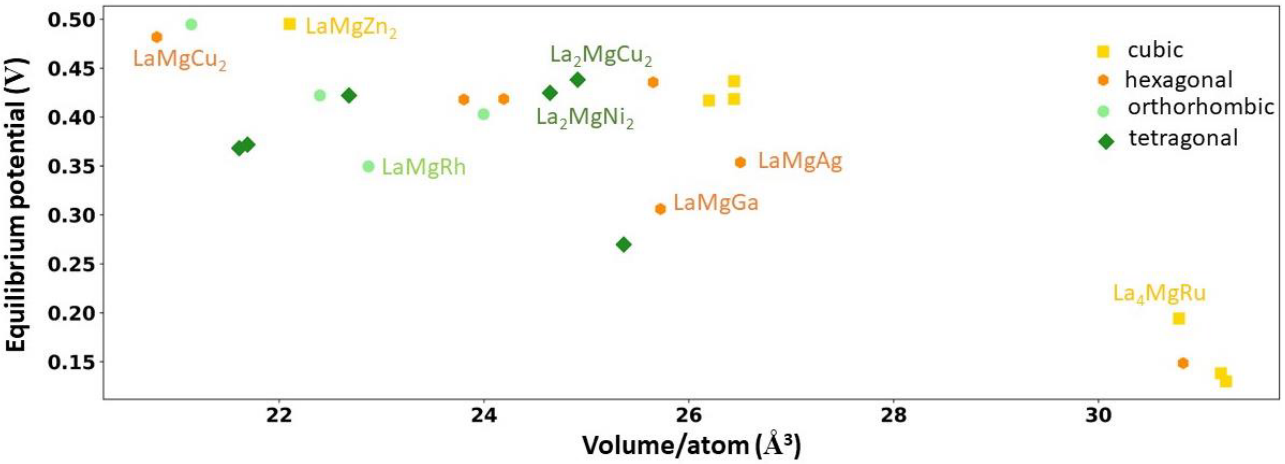

Figure 3. *La-Mg-containing intermetallics with predicted equilibrium potential in the 0.1-0.5V range; each point represents one of the 24 intermetallic compounds by crystal structure, while the formula is presented for the selected ones.*

We see that various intermetallics, formed with Mg and La, with or without the third element, are expected to provide suitable equilibrium potentials. In particular, Mg-La-Ir compounds and LaMg provide the smallest electrode potentials vs. Li^+/Li^0. La_4MgRu with a predicted potential of 0.19 V is a good choice, due to the known catalytic effect of noble metals in hydrogen sorption reactions. Intermetallics containing Cu, Zn, and Ni as a third element next to La and Mg are seen with higher potentials, near 0.5 V, in agreement with the known property of these metals to form less stable hydrides. Also important to note, while the potential is determined more by the chemical nature of the elements, intermetallics having various crystal structures have systematically different densities or volumes per atom, so all these aspects should be examined further to select those materials that will prove as the most stable in repeated charge/discharge cycles.

Conclusion

We present a screening study aimed at finding novel conversion-type anode materials for Li-ion batteries. We combine DFT and machine learning with domain knowledge to narrow the search for Mg-containing intermetallics. A total of 437 intermetallic compounds are identified in the Materials project database. Using structural data as input for the graph neural network-based machine learning model, we predict equilibrium potential vs. Li^+/Li^0 and found that 245 intermetallics satisfy the requirement of having his potential in the 0.1-0.5V range. We identify Ba, Ca, Ce, La, Sr, Sc, and Nd as suitable alloying elements for Mg, and point out some of the selected La-Mg-containing ternary intermetallics.

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