PERSPECTIVE

MATERIALS SCIENCE

Structure units as materials genes in cathode materials for lithium-ion batteries

Jiaxin Zheng[*], *Yaokun Ye, and Feng Pan*[*]

School of Advanced Materials, Peking University, Shenzhen Graduate School, China.

*Corresponding authors. Emails: zhengjx@pkusz.edu.cn and panfeng@pkusz.edu.cn

The basic structure unit of crystals is the lattice atom and its coordination environment. They are arranged periodically in certain combinations (e.g., space group) to form crystals. Generally speaking, the bonding interaction and electronic structure in the structure unit determine the intrinsic physical and chemical properties of crystals[1], similar to the key role of genes in lives. All the cathode materials for lithium-ion batteries (LIBs) can be formed by the combinations of Li, transition metal, and anion structure units (Fig. 1). For example, in olivine polyanion $LiFePO_4$ frameworks, FeO_6 octahedrons with Fe-O coordination bond are connected by sharing O corners to form a 2D network in *bc* plane, PO_4 tetrahedrons with strong P-O covalent bond are physically separated to connect adjunct FeO_6 planes, and LiO_6 octahedrons with Li-O ionic band are connected by sharing O corners to form a 1D channel on *b*-axis for Li-ion diffusion. Studying the physical and chemical properties of cathode materials from the perspective of the structure unit will lead to a better and

deeper understanding of the intrinsic electrochemical properties and provide guidance for the rational design of

which is detrimental to the electronic conductivity and finally affects the charge/discharge rate performance[3, 4]. The Li-ion transport in cathode materials is also closely correlated with the structure units and their arrangements. For example, the Li ions in layered $LiNi_xMn_yCo_zO_2$ (NMC) diffuse from one octahedral site (LiO_6) to another octahedral site, passing a gate site controlled by TM ions with one or two octahedral coordination(Fig. 2b) [5]. As a result, the migration of Li ions will be directly influenced by the valence state of TM ions and the size of TMO_6 and LiO_6/LiO_4. Using the above structure unit models, the predicted trend for the variation of Li-ion diffusion coefficient with the Ni content in NMC materials was verified by the experimental GITT measured results[5].

The structure stability of cathode materials is reported to be related to the structure units. For example, in $LiFePO_4$ crystal structure, the PO_4 tetrahedrons with strong P-O covalence act the joints to connect adjunct FeO_6 planes to establish the outstanding structure stability during electrochemical cycling. The distortion of TMO_6 in layered cathode materials during delithiation is the origin of structure disordering and phase transformation of crystal structures (Fig. 2c)[6, 7]. Besides the structure stability, the thermal stability of cathode materials also depends on the structure units. Using ab initio calculations, we previously proved that the oxygen structural units (TM_3-O-Li_x) of lattice oxygen in layered cathode materials determine the thermal stability[8], which can be tuned by changing the TM types and the number of Li-ions and modulating their positions in TM_3-O-Li_x (Fig. 2d). For example, the exchange of Ni and Li in Ni-rich NMC materials would form 180° Ni O Ni super-exchange

chains in TM_3-O-Li_x. □ □ □ □ □ □ □ □ -bonding with one Ni ion, and O ion between the spin anti- □ □ □ -bonding. This would enhance the thermal stability for Ni-rich NMC materials[7, 9]. The theoretically predicted thermal stabilities of NMC materials based on the above TM_3-O-Li_x unit models agree well with previous and our experimental measurements (in situ time-resolved X-ray diffraction and thermal gravimetric analysis)[8, 10]. Our recent experimental work combined with theoretical calculations reported that substitution of 1/3 NiO_6 with SbO_6 in $NaNiO_2$ to construct a highly ordered $(NiO_6)_6$ □ □ □ □ TM layers would enhance both the structure stability and thermal stability[11].

Most cathode materials are so-called charge-transfer materials, and the charge transfer process is correlated with the capacity and voltage of cathode materials. TM-ions were previously regarded as the sole sources of electrochemical activity in an intercalation cathode to provide the charge-compensating electrons after Li-ion extraction. The energy needed to oxidize TM^{n+} to $TM^{(n+1)+}$ is determined by energy levels of the TM *d* orbitals in TM units. For example, the energy required to remove an electron from the t_{2g} levels of octahedrally coordinated Mn^{4+} is significantly larger than that needed to remove an electron from t_{2g} levels of tetrahedrally coordinated Mn^{4+} (Fig. 2e) [12]. Recent observations have brought the above picture into question and argued that oxygen ions in oxide cathodes may also participate in the redox reaction[13]. With the top valence bands contributed by transition metal-ligand hybridization, it is not quite surprising that the oxygen O-2*p* states close to the Fermi level facilitates the reversible oxygen redox. Using DFT calculations with hybrid

functional HSE06 (which could correct SIE to some extent), Ceder *et al.* claimed that the oxygen redox in Li-rich layered cathode materials is originated from Li-excess in oxygen structure units (TM_3-O-Li_3) on the promotion of Li-O-Li O-2*p* non-bonding orbitals at the Fermi level (Fig. 2f) [14]. They further experimentally reported that using F substitution of O in Ni units in Li-rich layered cathode materials can lower the Ni^{3+}/Ni^{4+} to Ni^{2+} state, which not only increases the Ni redox reservoir but also preventing the compound from utilizing too much oxygen redox that can trigger oxygen loss[15]. A very recent important theoretical work proved that in Li-rich transition metal oxides, the reversibility of the anionic capacity is limited to a critical number of O holes per oxygen in TMO_6 units[16].

It should be noted that there also exists synergetic effect of various units. For example, the chemical potential for Li-ion storage in electrode materials at a certain temperature and pressure is determined by the synergetic effect between the kind of redox couples for TM units and the ionic bonding interaction in Li-ion units[17]. As discussed above, the migration of Li ions is also directly influenced by synergetic effect between TM units (TMO_x) and Li-ion units (LiO_x).

[Insert Fig. 2 here]

In summary, the structure units in cathode materials can be regarded as material genes, which determine the electronic conductivity, lithium-ion transport, structure and thermal stability, and charge transfer properties. Understanding the correlation between structure units and physical and chemical properties pushes the traditional electrochemistry in cathode materials for LIBs from a bulk/surface-based

interpretation to a more local chemical-bonding interpretation, where the local chemical coordination and local molecular orbitals dominate the physical and chemical properties. This provides an easy and direct guidance to improve the electrochemical performance of cathode materials or design high performance cathode materials by tuning the materials genes (like genetic engineering in biology). One way is to tune the materials genes directly. For example, substitution of TM and O with other elements in TMO_x units or breaking the symmetry of TMO_x by distortion or pressure would be effective ways to tune the electronic structure in cathode materials. The Li-ion diffusion can be tuned by substitution of TM with different valance state metals in TMO_x units and tuning sizes and arrangements of TMO_x units and LiO_x units. The other way is to search possible structures with high performance arising from the materials genes (Fig. 2g). First, a set of structure units must be chosen, and the number of times each structure unit appears within a single repeated unit cell is selected. Next, all the possible permutations of structure units are searched through with use of methods such as evolutionary algorithms, and the number of candidate structures is reduced by removing duplicates of the same arrangements. Finally, the relative stabilities of the left candidates were evaluated quantitatively by using ab initio calculations, and those final theoretical predicted stable structures are ranked according to some suitable selection criteria (e. g., energy density, stability, and rate performance) to give the most promising candidates for experimental synthesis.

FUNDING

This work was supported by the National Key R&D Program of China (2016YFB0700600), National Natural Science Foundation of China (21603007 and 51672012), Guangdong Key-lab Project (2017B0303010130), and Shenzhen Science and Technology Research Grant (ZDSYS20170728102618).

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Figure 1. The structure units in the representative cathode materials (olivine $LiTMPO_4$, spinel $LiTM_2O_4$, layered $LiTMO_2$, Li_2TMSiO_4) of LIBs (TM denotes transition metals).

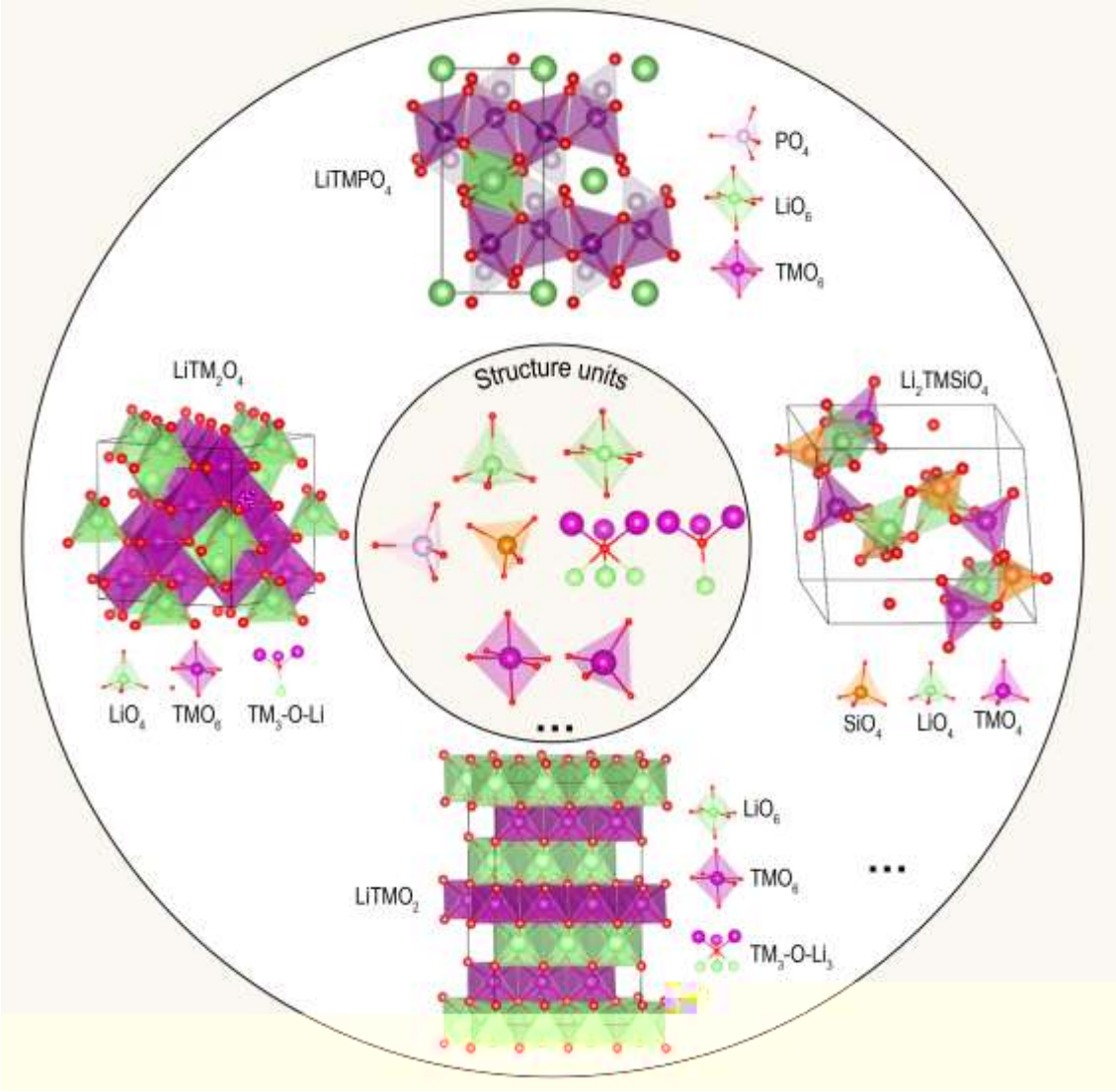

Figure 2. (a) Illustration of density of states and spin density (yellow) around TM atoms after delithiation with *x* content in $LiCoO_2$ and $LiFePO_4$, respectively. (b) The ODH (oxygen dumbbell hopping) and TSH (tetrahedral site hopping) types of the Li-ion diffusion pathways (right panel) in -$NaFeO_2$ type structure of layered cathode materials [5]. (c) Different distortion modes for an octahedral TM unit[6]. (d) A global view of tuning of thermal stability in layered NMC materials during delithiation [8]. (e) Energy levels of the Mn *d* orbitals in octahedral and tetrahedral coordinations [12]. (f) A Li-O-Li O-2*p* non-bonding orbitals near the Fermi level induced by Li-excess in oxygen structure units (TM_3-O-Li_3) [14]. (g) A schematic outlining the computational approach of searching possible structures arising from structure units. Different color modules denote different structure units [1].