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## Rational design of layered oxide materials for sodium-ion batteries

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**Abstract:** Sodium-ion batteries have captured widespread attention for grid-scale energy storage owing to the natural abundance of sodium. The performance of such batteries is limited by available electrode materials, especially for sodium-ion layered oxides, motivating the exploration of high compositional diversity. How the composition determines the structural chemistry is decisive for the electrochemical performance, but very challenging to predict especially for complex compositions. We introduce the “cationic potential” that captures the key interactions of layered materials, and makes it possible to predict the stacking structures. This is demonstrated through the rational design and preparation of layered electrode materials with improved performance. As the stacking structure determines the functional properties, this methodology offers a solution towards the design of alkali metal layered oxides.

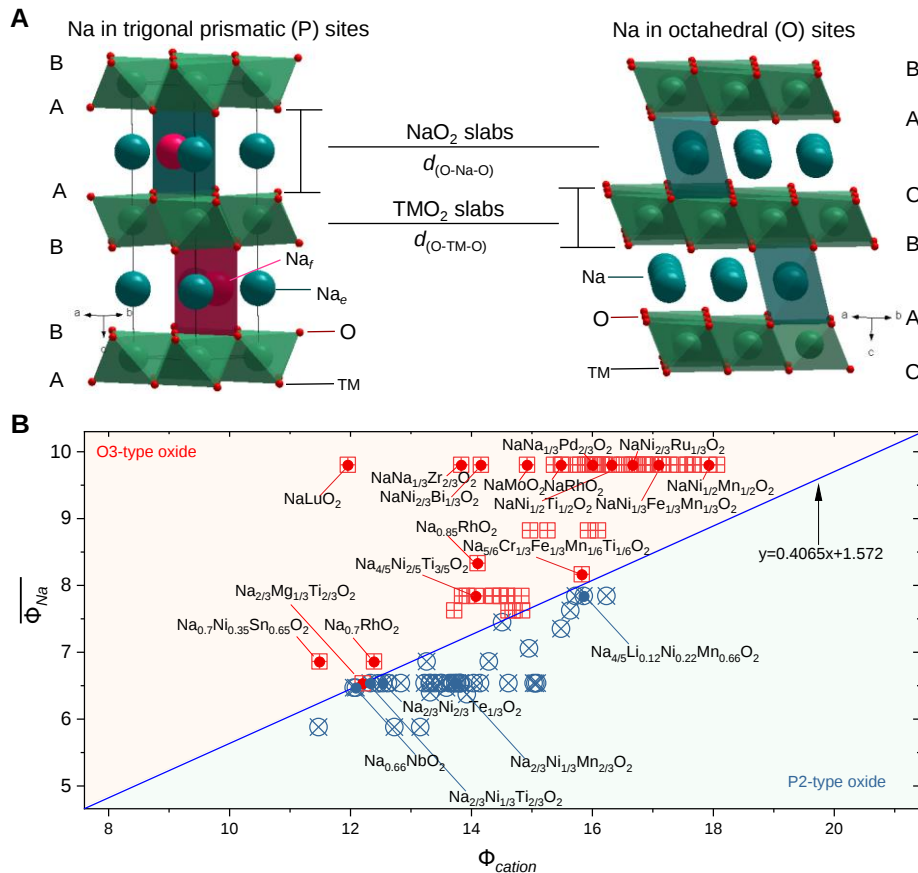
### One Sentence Summary:

A general strategy is proposed for the design of sodium-ion layered oxide materials.

Integration of intermittent renewable energy sources demands the development of sustainable electrical energy storage systems(1). Compared to lithium (Li)-ion batteries, the abundance and low cost of sodium (Na) make Na-ion batteries promising for smart grids and grid-scale applications(2, 3). Li-ion layered oxides, with the general formula  $\text{LiTMO}_2$ , have represented the dominant family of electrode materials for Li-ion batteries since 1980(4). Here TM stands for one or multiple transition metal elements that facilitate the redox reaction associated with Li-ion (de-)intercalation. The layered structures are built up by edge-sharing  $\text{TMO}_6$  octahedra, forming repeating layers between which Li ions are positioned in the octahedral (O) oxygen environment, leading to the so-called O-type stacking. The structure offers high compositional diversity, providing tuneable electrochemical performance, where well-known examples are  $\text{LiCoO}_2$  and Ni-rich  $\text{LiNi}_y\text{Co}_z\text{Mn}(\text{Al})_{1-y-z}\text{O}_2$ . In search of electrodes for Na-ion batteries, layered oxides ( $\text{Na}_x\text{TMO}_2$ ) offered the natural starting point(5). However, a key difference is that for Na-ion oxides in addition to O-type, P-type stacking can occur, where P-type refers to prismatic Na-ion coordination (Fig.1A). These stackings show distinctly different electrode performance, where the most studied layered stacking configurations are P2 and O3 types (Fig.1A), referring to the ABBA and ABCAB oxygen stacking, respectively(6). P2-type oxides usually provide higher Na-ion conductivity and better structural integrity against the O3 analogues, which is responsible for the high power density and good cycling stability(7). However, the lower initial Na content of P2-type electrodes limits the reversible capacity in the first charge compared to high Na-content O3-type materials(8). Usually, the structural transition between the O- and P-type can occur upon Na-ion (de)intercalation during (dis)charging, typically degrading cycle stability(2, 3).

In search for electrodes with good chemical/dynamic stability and high Na storage performance, various P2- and O3-type Na-ion layered oxides have been synthesized and investigated(9, 10). However, effective guidelines towards the design and preparation of optimal electrode materials are lacking. Crystal structures of P2- and O3-type layered oxides can be differentiated based on the ratio between the interlayer distance of the Na metal layer  $d_{(\text{O}-\text{Na}-\text{O})}$  and the TM layer distance  $d_{(\text{O}-\text{TM}-\text{O})}$ (11), where a ratio of  $\sim 1.62$  distinguishes P2- and O3-type oxides (Fig. S1 and Table S1)(12). The larger ratio of P2-type oxides, originates from the more localized electron distribution within the  $\text{TMO}_2$  slabs, which results in a weaker repulsion between the adjacent  $\text{NaO}_2$  slabs and consequentially a stronger repulsion between the adjacent  $\text{TMO}_2$  slabs. This hints that the electron

distribution plays an important role in the competition between the P- and O-type stackings in layered oxides.



**Fig. 1. Ionic potential and its use in Na-ion layered oxides. (A)** Schematic illustration of crystal representative P2-type (hexagonal) and O3-type (rhombohedral) layered oxides. **(B)** Cationic potential of representative P2- and O3-type Na-ion layered oxides, considering the Na content, oxidation state of transition metals and TMs composition (see Supplementary text and Fig. S3 for details).

Ionic potential ( $\Phi$ ) is an indicator of the charge density at the surface of an ion, which is the ratio of the charge number ( $n$ ) with the ion radius ( $R$ ) introduced by G. H. Cartledge<sup>(13)</sup>, reflecting the cation polarization power. The ionic potential shows the expected increase with oxidation state and atom mass (Fig. S2 and Table S2), a consequence of the less localized orbitals.

Aiming at a simple descriptor for layered oxides, we express the extent of the cation electron density and its polarizability, normalized to the ionic potential anion(O), by defining the “cationic potential”:

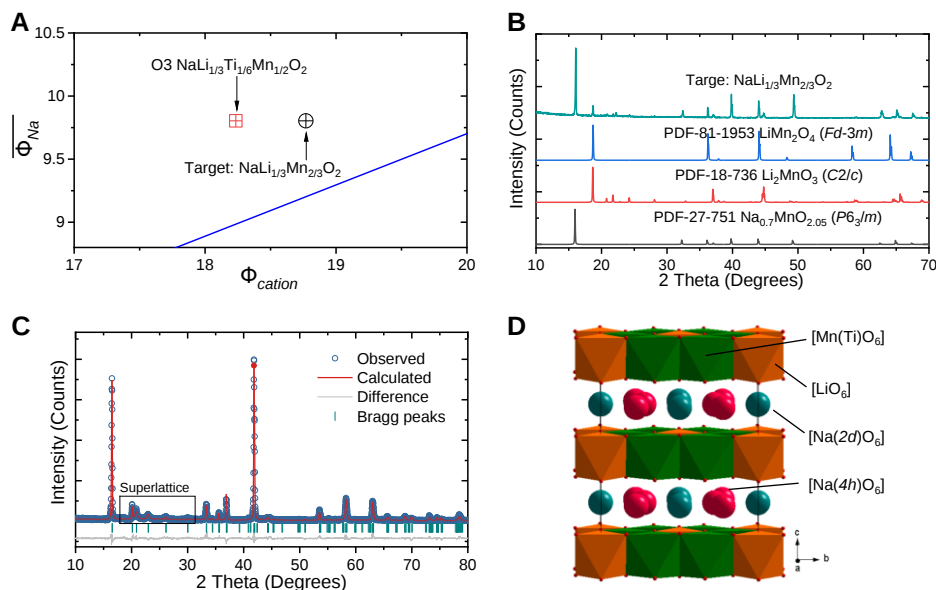
$$\Phi_{cation} = \frac{\Phi_{TM} \Phi_{Na}}{\Phi_O} \quad (1)$$

where  $\overline{\Phi_{TM}}$  represents the weighted average ionic potential of TMs, defined as  $\overline{\Phi_{TM}} = \sum \frac{w_i n_i}{R_i}$ ,  $w_i$  is the content of  $TM_i$  having charge number  $n_i$  and radius  $R_i$ , and  $\overline{\Phi_{Na}}$  represents the weighted average ionic potential of Na defined as  $\overline{\Phi_{Na}} = \frac{x}{R_{Na}}$ . Charge balance in  $Na_xTMO_2$  composition demands  $\sum w_i n_i = 4 - x$ , where  $x$  represents Na content and 4 is the total oxidation state to charge compensate  $O^{2-}$ .

The cationic potential  $\Phi_{cation}$  vs. the average Na ionic potential  $\overline{\Phi_{Na}}$  of reported P2- and O3-type layered oxides results in the phase map shown in Fig. 1B. The distinct P2 and O3-type regions indicate that the cationic potential is an accurate descriptor of the inter-slab interaction, and thereby the structural competition between P2- and O3-type structures. A larger cationic potential (Eq.1), implies stronger TM electron cloud extend and interlayer electrostatic repulsion resulting in the P2-type structure, with more covalent TM-O bonds and an increased  $d_{(O-Na-O)}$  distance (Fig. S4). Opposing this, a larger mean Na ionic potential, achieved by increasing Na content, increases the shielding of the electrostatic repulsion between the  $TMO_2$  slabs, favouring the O3-type structure.

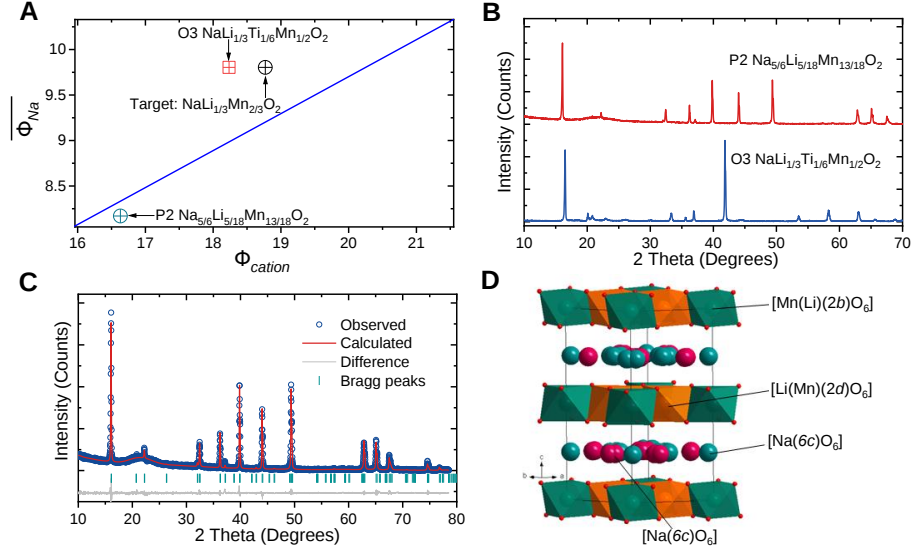
The phase map (Fig. 1B) shows that very small differences in TM or Na content can result in a transition between P2- and O3-type structures. To illustrate this we consider layered oxides with the composition  $Na_{2/3}TMO_2$ , which typically crystallizes in P2-type structure for the low Na content, such as P2- $Na_{2/3}CoO_2$ (14), P2- $Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$ (15), etc. However, replacing  $Ni^{2+}$  with  $Mg^{2+}$  in P2- $Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$ , facilitated by their similar ionic radii(16), leads to  $Na_{2/3}Mg_{1/3}Ti_{2/3}O_2$  for which the cationic potential predicts the O3-type structure, which is difficult to predict even with complex electrostatic energy calculations(15). In this case, the smaller ionic potential of  $Mg^{2+}$  against  $Ni^{2+}$  (Fig. 1B) decreases  $\Phi_{cation}$ ; the resulting lower covalence of Mg/Ti-O bonds increases the charge carried by the oxygens and thereby weakens the repulsion between the TM layers, resulting in O3-type structure (Fig. S5A and B, Table S6 and S7). Substituting 1/6  $Mg^{2+}$  by  $Ni^{2+}$  in  $Na_{2/3}Mg_{1/3}Ti_{2/3}O_2$  to  $Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$  moves it back into P2-type structure (Fig. S5B), illustrating how near these compositions are to the line separating the P2 and O3-type phases. Several other examples demonstrating that the proposed cationic potential approach captures the subtle balance between the P2- and O3-type layered  $Na_xTMO_2$  structures are provided in the Supplementary text, Fig. S5C and Fig. S6.

Delmas et al.(6, 17) used the Rouxel diagram(18) to distinguish  $Na_xTMO_2$  stacking structures, demonstrating that both Na content and the ionicity/covalence of bonds are the important factors. However, this method only accounts for the difference in Pauling's electronegativity (Fig. S7 and Table S4), that makes it impossible to predict the structure of oxides with the same TMs in different oxidation states(6, 17) (e.g.,  $Mn^{4+}$  and  $Mn^{3+}$  in  $Na_{0.7}MnO_2$ ) or for multiple-component systems (see Supplementary text, Fig. S8 and Table S5 for details). The cationic potential correctly predicts the stacking structure for these cases, providing a guideline for the development of Na-ion layered oxides.



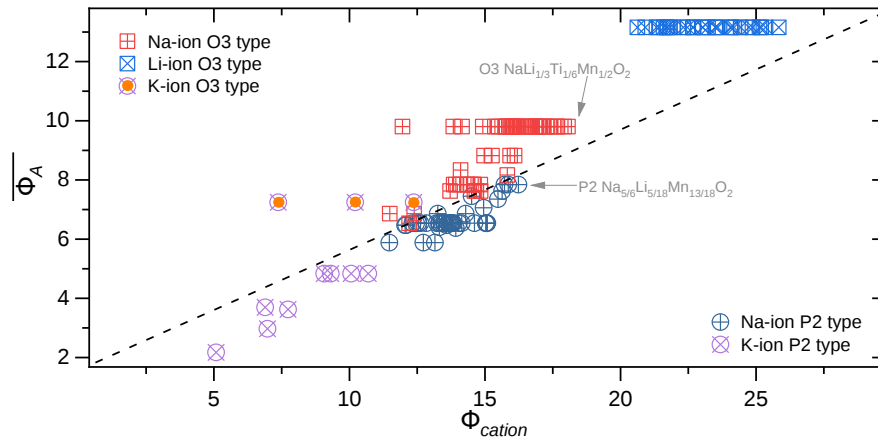
**Fig. 2. Designing an O3-type oxide. (A)** Analysis of the cationic potential of Na-Li-Mn(Ti)-O oxides (see Table S8 and S9 for details). **(B)** X-ray diffraction (XRD) patterns of the targeted  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  and the standard references. **(C)** Rietveld refinement of XRD pattern of  $\text{NaLi}_{1/3}\text{Ti}_{1/6}\text{Mn}_{1/2}\text{O}_2$  (see Table S10-12 for details). **(D)** Schematic illustration of the corresponding structure with the Li/Mn(Ti) ordering in the  $[\text{Li}_{1/3}\text{Ti}_{1/6}\text{Mn}_{1/2}]\text{O}_2$  slabs.

Using the cationic potential as guide, we design specific stacking structures by controlling the Na content and TM composition. An interesting starting point is  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$ , the analogue of  $\text{LiLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  ( $\text{Li}_2\text{MnO}_3$ ), providing capacity based on oxygen redox chemistry. This composition has not been prepared so far, despite that theoretical calculations argue  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  is stable in O3-type structure<sup>(19)</sup>. Various experimental conditions were attempted to prepare this composition in O3-type structure, but always a P2-type component, in addition to other phases was obtained. Lowering the cationic potential suggests that a possible route to prepare the O3-type structure is partial substitution of  $\text{Mn}^{4+}$  by  $\text{Ti}^{4+}$  (Fig. 2A), where  $\text{Ti}^{4+}$  has a lower ionic potential.  $\text{NaLi}_{1/3}\text{Ti}_{1/6}\text{Mn}_{1/2}\text{O}_2$  was successfully prepared in the predicted O3-type structure (Fig. 1B) by a typical solid-state reaction (see the Methods). Notably,  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  could not be synthesized as an O3-type structure using the same method (Fig. 2B). Rietveld refinement of the XRD pattern confirmed the layered rock-salt structure (Fig. 2C), in which the  $\text{NaO}_2$  layers alternate with the mixed  $[\text{Li}_{1/3}\text{Ti}_{1/6}\text{Mn}_{1/2}]\text{O}_2$  slabs (Fig. 2D). The  $(1/3, 1/3, l)$  superstructure peaks in  $20\text{--}30^\circ$  suggest Li/Mn(Ti) ordering in a honeycomb pattern, which is also confirmed by the aberration-corrected scanning transmission electron microscopy (Fig. S9). This ordered arrangement of Li and Mn(Ti) in the  $\text{TMO}_2$  slabs has not been observed in O3-type Na-ion oxides with exclusively 3d TMs. The electrochemical properties (see Supplementary text and Fig. S10A for details), demonstrate an higher energy density of  $\sim 630 \text{ Wh kg}^{-1}$  than the reported O3-type electrodes.



**Fig. 3. Designing P2-type oxide.** (A) Analysis of cationic potential of Na-Li-Mn-O oxides (see Table S13 and S14 for details). (B) XRD patterns of  $NaLi_{1/3}Ti_{1/6}Mn_{1/2}O_2$  and  $Na_{5/6}Li_{5/18}Mn_{13/18}O_2$  oxides. (C) Rietveld refinement of XRD pattern of  $Na_{5/6}Li_{5/18}Mn_{13/18}O_2$  (see Table S15-17 for details). (D) Schematic illustration of the corresponding structure with the Li/Mn ordering in the  $[Li_{5/18}Mn_{13/18}]O_2$  slabs.

We then use cationic potential to design a P2-type structure aiming at an anomalous high Na-content of  $x > 0.67$ , again starting from  $NaLi_{1/3}Mn_{2/3}O_2$ . To avoid formation of O3-type structure, the dividing line in Fig. 1B demonstrates that we should increase the cationic potential (Eq.1), assuming that Na content remains constant, which can be realized by increasing the ionic potential at TM sites. Based on the cationic potential, a P2-type structure with  $x=1$  ( $\overline{\Phi_{Na}} = 9.8$ ) will demand an extremely large TM ionic potential (larger than that of  $Mn^{4+}$ , having the largest value among the widely used TMs). Therefore, the Na content in  $NaLi_{1/3}Mn_{2/3}O_2$  should be lowered, which can be achieved through charge compensation by decreasing the Li and increasing the Mn content. Following this route, the cationic potential predicts that high Na-content  $Na_{5/6}Li_{5/18}Mn_{13/18}O_2$  composition should have the P2-type structure (Fig. 3A), which was indeed successfully prepared (Fig. 3B). So far, layered oxides prepared with such high Na content usually crystallize as O3-type structure. Compared to the O3-type  $NaLi_{1/3}Ti_{1/6}Mn_{1/2}O_2$ , the (002) peak of P2-type structure shifts towards lower diffraction angles, indicating that the expected increase in the  $c$ -axis of the unit cell (Fig. 3B). Rietveld refinement of the XRD pattern reveals that this P2-type layered structure can be indexed in the hexagonal  $P6_3$  space group (Fig. 3C, D). The electron energy loss spectroscopy mapping reveals a uniform distribution of the Na, Mn, and O elements in the plate-like particles (Fig. S11). Importantly, this as-prepared high Na-content material has significantly higher capacity of  $>200$  mAh  $g^{-1}$  (Fig. S10B).



**Fig. 4. Cationic potential phase map for layered alkali metal oxides.** Summary of reported layered alkali metal materials including Li-/Na-/K-ion oxides (see Table S18 and S19 for details).

Extending the cationic potential to other alkali metal layered oxides, Li-ion (Fig. S12) and K-ion (Fig. S13), results in phase maps shown in Fig. 4. The cationic potential (Eq.1), is found to increase from K- to Na- to Li-ion owing to the increasing ability to shield the TMO<sub>2</sub> interslab interaction. As a consequence, K<sub>x</sub>TMO<sub>2</sub> mainly crystallizes as P2-type and Li<sub>x</sub>TMO<sub>2</sub> as the O3-type structure, whereas Na<sub>x</sub>TMO<sub>2</sub> is the most interesting family as the shielding strength is at the tipping point between P2- and O3-type structures. The distribution of reported layered electrodes exhibits a clear trend by clustering around the dividing line (Fig. 4). For more than 100,000 new compositions, up to quaternary compositions on the TM position, the cationic potential is used to predict the most stable stacking structure, resulting in a distribution of compositions in the phase map around the dividing line (see Fig. S14, S15, and supplementary text for details). This demonstrates how the cationic potential can be used to predict the structure of new Na<sub>x</sub>TMO<sub>2</sub> layered materials, based on specific compositional demands. It is worth noting that the other parts far away from the line may also lead to other types of TM-oxide phases (e.g., rocksalt, spinel, etc.), or may not lead to stable structures at all, which is subject of ongoing investigations.

In summary, the ionic potential is a measure of the polarization of ions, mainly reflecting the influence of electrostatic energy on the system. Since the main difference between P- and O-type structures is the electrostatic polarization between AO<sub>2</sub> (A = alkali metals) and TMO<sub>2</sub> slabs, we can apply the proposed cationic potential method to distinguish and design materials, especially useful for Na-ion layered oxides. It should be noted that for entropy dominated phases, disordered compounds resulting from mechanical milling(20), or oxides prepared under particular conditions(21, 22), metastable structures or non-equilibrium phases(23), as well as the local distortion of TMs (e.g., due to Jahn-Teller effect on Mn<sup>3+</sup>), the ionic potential approach does not provide a sensible guideline. Moreover, the cationic potential only predicts if the proposed material will crystallize in P- or O-type structure, and one composition has only one structure. Because the actual obtained phases depend strongly on the nature of precursors and the conditions/atmosphere of thermal treatment, etc., which may cause the difference in stoichiometry and dynamic process, leading to structural changes. Further structural information is required to decide whether the corresponding material is stable/synthesizable in practice and calls for extensive investigation. Additionally, prediction of stacking structures is rather challenging for density functional theory

methods because the difficulty to predict the localized nature of TM orbitals, and especially for complicated TM compositions that have an enormous configurational space. We demonstrated the use of ionic potentials to tune the  $\text{TMO}_2$  interslab interaction, contributing to the important categories of layered materials. The currently known layered materials are either low Na-content ( $x=2/3$ ) P2-type oxides or high Na-content ( $x=1$ ) O3-type oxides, we suggest further exploration of high Na-content P2-type oxides and low Na-content O3-type oxides through the as-proposed cationic potential.

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## Supplementary Materials:

Materials and Methods

Supplementary Text

Figures S1-S15

Tables S1-S19

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