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# Cumulative cationic and anionic redox reaction in $\text{Mg}_3\text{V}_2(\text{SiO}_4)_3$ and impact on the battery performance

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## HIGHLIGHTS

- A reversible cationic and anionic redox is achievable with  $\text{Mg}_x\text{V}_2(\text{SiO}_4)_3$  ( $0 \leq x \leq 3$ ).
- Three-dimensional corner-shared polyanionic framework retains minimal structural changes.
- Low energy barrier for Mg-ion migration is obtained within  $\text{V}_2(\text{SiO}_4)$  host.

## ARTICLE INFO

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## ABSTRACT

A cumulative cationic and oxygen anionic redox reaction receives much attention for enhancing battery capacity in intercalant-excess cathode materials. However, such combinatorial electrochemical reactions are studied mostly for Li-containing cathode active materials so far, and multivalent systems remain unexplored from this perspective. Here, we examine the redox chemistry in the garnet-type  $\text{Mg}_3\text{V}_2(\text{SiO}_4)_3$  based on first-principles density functional theory calculations. Our calculations demonstrate the occurrence of a cumulative reversible cationic and anionic redox reaction without additional magnesium atoms, which offers an average discharge voltage of 3.23 V vs.  $\text{Mg}/\text{Mg}^{2+}$  with an energy density of as high as 1152 Wh/kg. Moreover, the unique three-dimensional corner-shared polyanionic framework in  $\text{Mg}_3\text{V}_2(\text{SiO}_4)_3$  only provides marginal structural changes, unlike layered Li-rich cathodes, which implies that irreversible  $\text{O}_2$  gas release is highly unlikely. Together with a low energy barrier for Mg migration, our finding provides a new insight to develop high-performance multivalent cathode active materials for which a cumulative cationic and oxygen anionic redox reaction plays an important role.

## 1. Introduction

Classical cationic redox reaction occurring in transition metals (TMs) has been a central operating principle for battery cathode materials including  $\text{LiCoO}_2$  and its variants such as  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$  since they were first developed. Despite the remarkable improvements achieved in cathode materials over the past decades, the demand for developing high energy density cathode active materials is exponentially growing due to the massive deployments of large-scale energy storage systems in various applications. For instance, the global electric vehicle stock is projected to jump to 140 million automobiles by 2030 (i.e., 30% annual growth rate) under the stated policies scenario, requiring the automotive battery capacity increase to 1.5 TWh per year in 2030 [1].

Among numerous attempts to develop high-capacity cathode materials, a novel approach based on an oxygen anionic redox reaction has recently received much attention because intercalant-excess hosts can make further (de)intercalations of working-ions achievable. For example, compared to a well-known  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  cathode (NMC 111) with a rechargeable capacity of 150 mAh/g in 3.5–4.2 V against Li metal anode [2], a Li-rich cathode,  $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$  ( $x = 1/3$ ), delivers a greater capacity of 220 mAh/g in 2.0–4.6 V through additional substitution of transition metals by Li in the metallic layer besides the original Li present in TM interlayer. In the excessive Li condition, the improved battery performance was shown to arise from the anionic redox reaction by oxygen [3].

However, subsequent studies have shown that the oxygen redox

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