Mass Transfer of Divalent Ions in an Oxide Host: Comparison of Mg²⁺ and Zn²⁺ Diffusion in Hexagonal K_xW₃O₉ Bronze

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ABSTRACT. Pure and isovalent-cation substituted potassium hexagonal tungsten bronze (KHTB) have been synthesized and used as a model oxide host to study the electrochemically driven bulk diffusion of divalent Mg^{2+} and Zn^{2+} ions. For the cation-substitution, tungsten has been replaced by 10% Mo or 5% Cr as a strategy to mitigate the slow diffusivities of the divalent ions. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies reveal the superior kinetics of Zn^{2+} insertion compared to that of Mg^{2+} , majorly due to the sluggish desolvation/electro-adsorption of Mg-species at the electrode-electrolyte interface in an organohaloaluminate-based electrolyte. For both divalent cations, the insertion/extraction kinetics exhibits a profound improvement with the isovalent-cation-substituted KHTB phases due to the synergistic effect of particle size reduction and enhanced ionic diffusivities. Hence, maximum insertion amounts of o.18 and o.20 moles, respectively, for Mg^{2+} and Zn^{2+} per ($W_{1+x}M_x$)₃O₉ formula unit (M = Mo or Cr) have been achieved within the electrolyte stability window, whereas the unsubstituted KHTB is essentially inactive. Further EIS studies in symmetric cells indicated the inherently faster kinetics of Zn^{2+} diffusion compared to that of Mg^{2+} in identical hosts. Calculations based on Density Functional Theory (DFT) were implemented to probe the local atomic environment of the diffusing ions. The DFT study suggests that the Zn-ion transition-state is stabilized by ~ 0.4 eV compared to that of Mg^{2+} through a host-to-guest charge transfer, a consequence of the tendency of Zn^{2+} ions to form covalent bonds compared to Mg^{2+} with the oxide anion.

INTRODUCTION

With the surge in the use of batteries for mobile and stationary applications, electrochemical energy storage devices based on multivalent (MV) ions have gained a great deal of renewed interest.¹⁻¹⁰ Among the post Li-ion technologies and multivalent ion batteries, Mg²⁺ and Zn²⁺ have been proposed as two promising platforms to be invoked as the working ion in insertion host materials. This is due to the abundance, cost, environmental benignity, bio-friendliness and above all, a high theoretical volumetric capacity.¹¹⁻¹³ Moreover, due to the electropositive nature of Mg and to a lesser extent Zn as well as a dendrite-free electroplating¹⁴ from organometallic reagents, they can be directly used as negative electrodes in a full cell setup, unlike the problematic Li and Na counterparts.

Given the obvious advantages of using the aforementioned MV ions, the lack of suitable host cathodes that can incorporate Mg²⁺ and Zn²⁺ ions in their lattice in a topotactic pathway has severely hampered the advance in the field.¹⁵ Among the very limited pool of host materials, a handful of examples from sulfides, polyanionic materials, and oxides can be mentioned.^{9,11,16–22} Multivalent ion insertion/extraction into/from transition metal oxide (TMO) hosts is not a straightforward task, and a review of the literature reveals often varying and occasionally

opposing reports of electrochemical activity of the respective phases. To add to the difficulty, lack of compatible electrolytes with metallic Mg anode, corrosive electrolyte salts especially at anodic voltages, use of pseudoreference electrodes, etc., makes independent verification of the reported work challenging. More often than not, Mg²⁺ insertion in TMO were made possible via extensive downsizing of the cathode active material, where pseudo-capacitance and surface electro-adsorption become significant.²³⁻²⁵ Also addition of H₂O in the socalled "wet electrolyte" to screen the charge of Mg²⁺ ion has been attempted as another strategy to mitigate the sluggish diffusion of MV ions.24,26,27 Although successful, this has raised questions regarding the compatibility of the cell component as well as causing parasitic competitive reactions such as proton insertion.²⁸ Due to the last two major issues, reports of the true "bulk diffusion" of MV ions in macro-sized TMO hosts in dry electrolytes is not frequently encountered in the literature. As a result, our understanding of pure bulk diffusion of MV ions in TMO hosts lacks severely behind that of the monovalent analogs.

The aim of the current work is to shed light on the underlying principles of Mg²⁺ and Zn²⁺ diffusion in an oxide host, potassium hexagonal tungsten bronze (KHTB),

 $K_x W_3 O_9$ (0.1 $\leq x \leq 1$). In regard to the intercalation chemistry of tungsten trioxide family, previously electrochemical insertion of monovalent cations into HTB related phases have been tried.^{29,30} With respect to Mg²⁺ insertion into monoclinic WO₃ and HTB, chemical insertion of Mg²⁺ from organomagnesium reagents have been attempted three decades ago with the aim to establish an analogy with the monovalent ion insertion.^{31,32} The latter studies achieved insertion compounds of magnesium with nominal compositions of Mg_{0.08}WO₃ and Mg_{0.45}W₃O₉, respectively, for the monoclinic and HTB polymorphs. Also, electrochemically driven Mg2+ insertion into monoclinic WO3 using Mg anode and a nonaqueous electrolytes has reported an insertion of 0.5 moles of Mg per WO₃ formula unit (115 mAh.g⁻¹).³³ Nevertheless, the reported capacity was based upon the coulometric measurement using an electrochemical setup comprising Mg(ClO₄)₂/THF electrolyte, which is known to form a passive film on Mg anode with an ensuing large Mg stripping overpotential and the possibility of side reactions.34 Likewise, electrochemical Zn2+ insertion into monoclinic WO₃ has been attempted, which exhibits multiple monophasic and biphasic regions below 0.6 V (vs. Zn^{2+}/Zn) in the voltage-composition profile, yielding Zn_{0.3}WO₃ as the maximum degree of insertion.³⁵ Recently, another study of electrochemical Mg2+ insertion into monoclinic and layered $WO_3.nH_2O$ (n = 1,2) has been published, targeting the role of crystal water molecules on the magnesium intercalation properties from a kinetic standpoint.³⁶ The study suggests that among the anhydrous and hydrated WO₃ phases, the anhydrous phase exhibit the highest capacity for Mg insertion of up to Mg_{0.3}WO₃, with the hydrated phases outperforming at higher rates. The results of the last study stands in line with the earlier work³³ as significant amounts of Mg²⁺ can be inserted into monoclinic WO₃, despite that there are unclear points regarding the method of the potential referencing and the choice of a capacitive counter electrode.

Despite a similarity in composition, the hexagonal WO₃ is structurally and chemically different from the monoclinic analog. The former, with some inserted ions as in KHTB, exhibits metallic conductivity with large hexagonal ionic diffusion channels. These features are essential for the ionic diffusion involving multivalent ions, as the difficulty of overcoming the ion-hopping energy barrier and the associated electronic charge redistribution between the adjacent transition metals is known to be the major cause of the lack of activity in the most known oxide hosts. Therefore, exploration of KHTB is a good choice as a model oxide host for the sake of studying the diffusivities of multivalent ions, despite its low theoretical gravimetric capacity (one electron per W_3O_9 with 38 mAh.g⁻¹). Given that the earlier electrochemical insertion studies on tungsten trioxide dealt with the monoclinic form, such a study also serves to fill the gap in the existing knowledge.

Here, we present the electrochemical insertion of Mg^{2+} and Zn^{2+} into pure, Cr- and Mo-substituted KHTB hosts. In each case, the insertion behavior is studied with a variety of potentiostatic and electrodynamic techniques. The results suggest that in full cells, electro-adsorption of monovalent magnesium-containing species on the anode-electrolyte interface adversely affects the Mg-ion cell performance in comparison to the zinc cell. Also, ionic diffusion studies in symmetric cells suggest Zn^{2+} bulk diffusion is more facile than that of the Mg²⁺ counterpart. A combination of x-ray crystallography and Density Functional Theory (DFT) calculations to probe the diffusion mechanism of the divalent ions indicates that the better diffusivity of Zn^{2+} ions emanates from a higher covalency of Zn^{2+} —O²⁻ interactions.

EXPERIMENTAL

Materials: WO₃ (ACROS Organics, 99+ %), MoO₃ (Sigma-Aldrich, reagent grade, \geq 99.5 %), K₂Cr₂O₇ (Sigma-Aldrich, reagent grade, \geq 99.0 %), KI (Sigma-Aldrich, reagent grade, \geq 99 %), Na₂S₂O₈ (Sigma-Aldrich, reagent grade, \geq 98 %), Zn(CF₃SO₃)₂ (ACROS Organics, 98 %), AlCl₃ (Sigma-Aldrich, anhydrous, powder, 99.999 % trace metals basis), ethyl magnesium chloride (Sigma-Aldrich, 2M in THF), Mg(ClO₄)₂ (Sigma-Aldrich, reagent grade), THF (Alfa Aesar, \geq 99.8 %), Mg foil (Alfa Aesar, 99.9 %), and Zn shots (Alfa Aesar, 99.99 %) were used as received. Acetonitrile (Sigma-Aldrich, anhydrous, 99.8 %) was further dehydrated with a molecular sieve (4 Å).

Synthesis: Pure and doped hexagonal KW₃O₉ were prepared by a slightly modified molten salt method as reported previously.³⁷ In each case, 0.6955 g (3.0 mmoles) of WO_3 was ground and mixed with 3.3200 g (20 mmoles) of KI in a mortar and pestle, transferred into a quartz tube, and heated at 730 °C for 6 h under flowing Ar. For the Cr- or Mo-doped samples, 0.0203 g K₂Cr₂O₇ (0.075 mmole) and 0.0432 g of MoO₃ (0.3 mmole) were mixed, respectively, with 2.95 and 2.90 mmoles WO₃ to yield $K(W_{0.95}Cr_{0.05})_{3}O_{9}$ nominal compositions and $K(W_{0.90}Mo_{0.10})_{3}O_{9}$. After the completion of reaction, the quartz tube contents were extracted by washing with deionized (DI) water, filtered, and dried under ambient conditions. Then the samples were analyzed for phase purity by X-ray diffraction (XRD).

The as-prepared pure and substituted KHTB samples were then ground in a mortar and pestle and subjected to a topotactic oxidative K⁺ removal with $Na_2S_2O_8$ (2:1 mole ratio) under hydrothermal conditions at 180 °C for 12 h. The oxidized phases were collected by filtration, washed thoroughly with DI water to remove the unreacted persulfate and reaction products, dried, and checked for phase identity with XRD.

Materials Characterization: Powder XRD patterns of the as-prepared and processed phases were recorded with a Rigaku Miniflex diffractometer, equipped with a graphite crystal monochromatized Cu K_{α} source. All diffraction patterns for phase quality checking were obtained with a scan rate of 0.06° min⁻¹, except for the crystallographic analyses after electrochemical insertion tests, where the scan rate was reduced to 0.015° min⁻¹. Scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) imaging and analyses were performed with a JEOL JSM-5610 microscope equipped with an Oxford Instruments Peltier-cooled EDS detector. Magnetic measurements were carried out with a Quantum Design DynaCool PPMS system using a Vibrating Sample Magnetometer (VSM) measuring module.

Electrode Preparation and Electrochemical Testing: The oxidized KHTB samples were first ground in a planetary ball mill in a stainless-steel jar and balls at 300 rpm for 5 h for the particle size reduction. The powders mixed with Super P conductive carbon and PVDF in the mass ratio of 70 : 15 : 15, followed by the addition of an appropriate amount of N-methyl-2-pyrrolidone (NMP) to dissolve the PVDF. The resultant cathode slurry was applied onto aluminum sheets as a film of uniform thickness and dried under vacuum in an oven at 150 °C for 12 h. Due to the severe Al corrosion in Mg- and Zn-ion electrolytes under anodic conditions, freestanding electrodes of the cathodes were obtained by dissolving the Al layer completely in 5% (by wt.) hydrochloric acid. It is well known that the bronze phases of tungsten trioxide are notoriously resistant against the chemical attack by strong acids.³⁸ Therefore, no electrode dissolution was expected because of acid treatment, as confirmed through XRD analysis subsequently. The resultant high mass-loading, free-standing electrodes (~ 15 mg.cm⁻²) were cut and transferred into an Ar-filled glove box (O2, $H_2O < 0.1$ ppm) and standard 2032 type coin-cells were assembled. In each case, a metallic foil of Mg or Zn was used as the anode, a 0.4 M 2 : 1 ethylmagnesium chloride—AlCl₃ in THF [0.5 M Zn(CF₃SO₃)₂ in acetonitrile] as the electrolyte, and glass fiber membranes as the separator. A Biologic VMP potentiostat was used for the electrochemical impedance spectroscopy (EIS) analyses, while a CHI 760C or a µMetrOhm type III were used for cyclic voltammetry analyses (scan rate: $50 \mu V.s^{-1}$). Finally, galvanostatic charge-discharge curves or linear sweep scans were obtained with an Arbin Instrument battery cycler model BT 2000. For the post-reduction analysis, the electrodes in the discharged state were recovered from the de-crimped cells, washed and rinsed several times with anhydrous acetonitrile, and then dried before transferring immediately to XRD analysis.

Chronopotentiometric measurements of permanganate decay rate: In order to measure the relative diffusivities of Mg^{2+} and Zn^{2+} in the KHTB host, $K_{0.25}(W_{0.95}Cr_{0.05})_3O_9$ has been electrochemically reduced with Mg^{2+} and Zn^{2+} ions at a constant potential of 10 mV (vs. metallic anodes) for 42 hours (Figure S1(a)). The cells were then de-crimped and the KHTB electrodes were washed with THF, acetonitrile, ethanol and DI water to

remove the electrolyte. Next, the electrodes were placed in a sealed three-neck round bottom flask containing 30 mL of a concentrated sulfuric acid (2 N) aqueous solution and purged continuously by the Ar gas to avoid air oxidation. Finally, an appropriate amount of 1 N KMnO₄ solution (o.5 eq of MnO_4 per 1 eq of M in $M_xK_{0.25}(W_{0.95}Cr_{0.05})_3O_9$, M: Mg, Zn) was delivered using a micropipette, to the container and stirred using a magnet bar so that the inserted ions are extracted via an oxidative deintercalation. The potential of the solution then recorded using an inert Pt working electrode (vs. saturated AgCl/Ag reference) as a function of the time. The above oxidant : reductant ratio allows the oxidizer to be consumed quantitatively, thus a sharp reduction in the solution potential can be recorded. Details of the reaction and thermodynamic potential of the system are provided in the SI, with a schematic of the setup given in Figure $S_1(b)$.

Computational Method: Theoretical calculations of the various Mg/Zn insertion site energy in K_{0.5}W₃O₉ were carried out at the DFT level using the Quantum Espresso (QE) plane-wave code.³⁹ In each case, the electronic wavefunction has been obtained using Projector Augmented Wave (PAW) functionals with Generalized Gradient Approximation (GGA) exchange-correlation correction, as parameterized according to the PBE method.40 All calculations were performed in a $2 \times 2 \times 1$ supercell (Z = 12) with a 540 eV kinetic energy cutoff for the electronic waves and the K-space was sampled through a uniformly spaced $2 \times 2 \times 3$ grid, generated by Monkhorst-Pack method.⁴¹ Despite the heavy nature of W atoms, scalarrelativistic functionals were used (i.e., no spin-orbit coupling), only allowing spin polarization as in this specific structure the electrons close to the Fermi level are not bound to local atomic orbitals of W atoms at the ground state (see below). The activation energy barriers to ionic conductivity were calculated first by the identification of the Zn insertion sites in the KHTB via Pawley refinement and Fourier difference map synthesis using the GSAS-II suite,⁴² and further expanded by locating the transitionstates and local minima on the potential energy surface (PES). In order to improve the accuracy of the activation energy estimation, climbing image nudged elastic band (CI-NEB) routine of the QE package was implemented. Details of the input selection for the theoretical voltage calculations and activation energies are provided in Figures S11-S13 of the Supporting Information. Finally, crystal orbital Hamilton population (COHP) analysis was performed on the relaxed eigenfunctions of the DFT system using the LOBSTER code.43

RESULTS AND DISCUSSION

 KW_3O_9 was obtained as the product of reductive K⁺ insertion into WO₃ host, where the iodide acts as a reducing agent with subsequent release of I₂ gas. At the synthesis temperature (730 °C), WO₃ adopts an orthorhombic structure, with heavily distorted WO₆ octahedra in a geometry similar to the ABO₃ perovskite with vacant A cation sites. Unlike the case of smaller alkali ions, K⁺ ion is too large to yield a perovskite-type KWO₃ (tolerance fac $tor^{44} = \sqrt{2r_{K-0}/2r_{W-0}} = 1.70 >> 1.0$; thus, the non-topotactic K⁺ insertion follows a complete phase transformation into the hexagonal system. Similar to the perovskite structure, the W atoms preserve the octahedral environment connected through corner sharing. On the other hand, K⁺ ion also maintains its coordination number of 12 as in the ideal perovskite, but rearranged in a hexagonal prism environment rather than in a cuboctahedron. Such a structural rearrangement creates clusters comprised of WO₃ triplets as the crystal building blocks, forming large hexagonal channels that are filled with K⁺ ions (site 2b) and smaller empty trigonal channels (site 4d), along the [001] direction. This geometry along with the covalent nature of W-O bond creates delocalized energy bands, which are partially filled with the electrons balancing the guest ion charge. Figure 1(a) depicts the XRD pattern of the as-synthesized hexagonal K_{0.75}W₃O₉, indexed in the hexagonal crystal system (S.G. P6₃/mcm). Figure 1(b) shows the DFT derived overall density of states (DOS) for the typical composition K_{0.5}W₃O₉, confirming the non-magnetic, metallic nature of the solid. Figure 1(c) shows the local structure of the W₃O₉ cluster, along with the graphical representation of the bands at the Fermi level (*i.e.*, valence band). From Figure 1(c), it is evident that the valence band of KHTB has a significant t_{2g} character; this is in line with the classical picture derived from crystal field theory, as a result of t_{2g} - eg splitting in the octahedral field, with the electron populated into the low-lying t₂₀ band where it is delocalized over the entire crystal. Previous studies of optical, electronic, and magnetic properties of AW_3O_9 (A = Li, Na, K, Rb, and Cs) clearly demonstrate that the physical properties of HTB solids are almost independent from the identity of the intercalated ion, thereby confirming the complete charge ionization of the intercalants.45

The chemical formula of the as-prepared and chemically oxidized KHTB samples were identified as, respectively, $K_{0.75\pm0.06}W_3O_9$, and $K_{0.25\pm0.02}W_3O_9$, based on EDS measurements (Figure S2).

Magnetic studies exhibit another aspect of the delocalized nature of electronic waves within the KHTB structure. Figure 2 depicts the molar susceptibilities of $K_{0.75}W_3O_9$ and the chemically oxidized $K_{0.25}W_3O_9$ as a function of temperature (red and blue traces). Both samples exhibit a weak magnetic response, which becomes essentially temperature independent at temperatures greater than 100 K. As previously reported, this small paramagnetic response can be ascribed only to the magnetization of a free electron gas, *i.e.*, Pauli paramagnetism.⁴⁵



Figure 1. (a) X-ray diffraction pattern of the pristine $K_{0.75}W_3O_9$ phase indexed in the hexagonal setting; the inset shows the crystal structure as viewed along the [001] direction. (b) Calculated spin-polarized band diagram of $K_{0.75}W_3O_9$. (c) Depiction of the atomic orbitals contributing to the metallic valence band of $K_{0.75}W_3O_9$.

The low-temperature response of the magnetic susceptibility also contains information regarding the average oxidation state of the W atoms (Figure 2 inset). It is known that the HTB phases exhibit superconductivity at low temperatures (hence a diamagnetic state), while the critical temperature increases as the electron density decreases.⁴⁶⁻⁴⁸ Therefore, the oxidative removal of the K⁺ ions from KHTB by the action of Na₂S₂O₈ is evident, as the superconducting state critical temperature T_c has increased from less than 2 K in the pristine K_{0.75}W₃O₉ to 4.73 K in K_{0.25}W₃O₉. It should be mentioned that here oxidative removal of K⁺ from pure and doped KHTB phases has been attempted with the purpose of vacating some insertion sites for subsequent insertion of the divalent Mg²⁺ and Zn²⁺ ions. Considering the Cr- and Mo-doped KHTB phases, a visual inspection of the synthesis product reveals obvious color difference as compared to the pure KHTB phase; while pure KHTB has the characteristic dark blue color typical of the bronze phases, Mo- and Crsubstituted KHTB are, respectively, navy blue and emerald blue in color (Figure S₃).



Figure 2. Temperature dependence of the molar magnetic susceptibility of pristine and chemically oxidized pure KHTB and the pristine Cr-substituted KHTB. Inset shows the magnified view of the low-temperature regime.

At the same time, the molar magnetic susceptibility χ_m curve of the as-prepared K_{0.75}(W_{0.95}Cr_{0.05})₃O₉ phase in Figure 2 shows the usual paramagnetic response obeying the Curie-Weiss law, while the Mo-doped sample shows no significant difference compared to the pure KHTB phase (data not shown). It should be emphasized that such noticeable changes in optical and magnetic properties have been achieved by substituting only 5.0 % of tungsten by Cr atoms. This change in turn may be attributed to the limited dispersion and size of Cr 3d orbitals, which locally disrupts the continuous metallic band comprised by overlapping W 5d t_{2g} orbitals. As a result, substitution of W by Cr in KHTB instigates a number of interrelated modifications to the original material properties: (a) opening up a gap in the energy band structure, (b) loss of metallic conductivity and emergence of semiconducting behavior, (c) localization of electrons on atomic orbitals and appearance of Curie-Weiss (C-W) paramagnetism. On the same subject, it worth mentioning that the overall magnetic response of the Cr-substituted phase follows pure C-W behavior, rather than a C-W behavior superimposed on a fixed Pauli paramagnetic behavior (note the drop in the γ_m of the Cr-doped phase below that of the pure phase at $T \ge 50$ K). The magnetic response of the chemically-oxidized, Cr-doped phase exhibit the same trend (i.e. pure C-W paramagnetism) as shown in Figure S4.

From a multivalent-ion intercalation perspective, the ability to tune the electronic conduction without changing the host structural features is an informative tool as it allows decoupling the problem of charge redistribution from pure ionic diffusion, which are otherwise closely correlated. Furthermore, morphological inspection of the pure and substituted KHTP phases reveals that incorporation of Mo and Cr reduces the average particle size, presumably due to development of internal strain and crystal cleavage due to different sizes of the isovalent ions (Figure S5).

Initially, CV was used to assess the kinetics of Mg^{2+} and Zn^{2+} insertion into the pure and substituted KHTB phases. Also, CV tests were conducted on blank cells to determine the proper electrochemical window at which all cell components are stable and no parasitic current flows (Figure S6). Figure 3(a) shows the CV curve of Mg^{2+} insertion and extraction into and out of pure KHTB phase.

The CV started by scanning the potential from the open-circuit voltage (typically 1.7-1.9 V) towards the cathodic vertex (0.1 V vs. Mg²⁺), followed by reversing the sweep direction toward the upper vertex potential at 2.0 V. The CV curve has a symmetric shape, inferring the reversibility of the Mg²⁺ insertion/extraction process. However, the emergence of certain features such as spikes in the current (at 1.65 V and 0.6 V, respectively, for the cathodic and anodic scans) and the subsequent sluggish increase in the current vs. potential are notable. The plateau in the I-V curve with a negligible current flow at the beginning of either potential ramp represents the background capacitive current. Thus, the current spike and the subsequent sloppy current wave can be certainly assigned to the faradaic reaction of reversible partial reduction of W⁶⁺ to W⁵⁺ and neutralization of the negative charge by Mg²⁺ ions.

The shape of the I-V curve suggests that at potentials corresponding to the faradaic reaction, the current is alwavs under charge-transfer control and no evidence of diffusion control can be traced. This is mainly due to the fact that the current always increases with an increase in the applied overpotential and no current limiting factor, which leads to the appearance of a current peak, can be observed in either cathodic or anodic scans. For systems which are under diffusion-control, at high enough applied overpotentials (such as Figure 4(b)) there is a peak or a step in the I-V curves, respectively, due to a constant flux or depletion of the electroactive species. Furthermore, emergence of the sudden rise in the current has its route in the reaction mechanism and kinetics, receiving contributions from either the anode and cathode half reactions or both.

To inspect the nature of the processes governing the current flow in the Mg-ion full cell, staircase potentiostatic electrochemical impedance spectroscopy (SPEIS) was employed (Figure 3 (b) and (c)). Briefly, SPEIS superimposes the oscillating AC waveform on the pure DC staircase potential background so that a complete EIS curve can be recorded under DC step-potential sweep. Figure 3(b) and (c) depict the contour plots of the complex phase angle (color-coded) at each applied potential (abscissa) versus frequencies (ordinate) during the discharge (panel (b)) and charge (panel (c)) scans.

Here, the choice of using the impedance phase angle is based on its sensitivity to discriminate between capacitive and inductive behavior of an electrode. On the contour maps, the areas marked with a positive complex phase angle (red to orange in color) indicate an inductive behavior, whereas a negative phase corresponds to a capacitive current-limiting step at the applied potential. Evidently, under background current conditions (panel (b), 1.68 < E < 1.80 V, panel (c) 0.65 < E < 0.95 V) the EIS response represents a negative phase angle, indicating a pure capacitive behavior and lack of appreciable faradaic redox reactions. With an increase in polarization in either the anodic or cathodic direction, the current rise in the I-V curve (red trace in panels (b) and (c)), which is accompanied by a sudden change of the system EIS response from a capacitive into an inductive state as the phase angle suddenly switches from -40° to $+20^{\circ}$ (100 mHz). The inductive nature of the EIS response under faradaic current flow indicates that the Rate-Determining-Step (RDS) involves coupled chemical reactions and electro-adsorption of reaction intermediates on the surface(s) of one or both electrodes.49 This implies that the desolvation of magnesium species at the electrode-electrolyte interface is the slowest step in the sequence of Mg²⁺ insertion in KHTB. Previously, it has been shown that Mg electrostripping-electroplating in organohaloaluminate-based electrolytes follows a multistep electron-transfer process involving the Mg-containing species with an intermediate oxidation-state, electroadsorbed on the Mg surface, with the RDS being the desolvation and reduction of the electroadsorbed species to the metallic Mg adatom on the Mg substrate.^{12,50} Therefore, it is possible to conclude that in the current case, the inductive behavior of EIS is due to a slow redox reaction involving electroadsorbed Mg-species. This conclusion has an important consequence: the problem of Mg-species adsorption on the metallic Mg anode places an upper limit on the rate capabilities of Mg-ion batteries utilizing Mg anode in combination with organohaloaluminate-based electrolytes. The limiting effect of Mg-ion electro-adsorption becomes obvious when the overall reaction kinetics on the cathode occurs at a higher rate than the anode, as in the current case. The occurrence of Mg in the univalent state has been the subject of several studies previously.^{51,52}

Figure 4 (a) depicts the CV analysis of the behavior of the Mo, and Cr-substituted W₃O₉ electrodes toward Mg²⁺ insertion/extraction and its comparison against the pure KHTB sample. Such comparisons are notably useful to illustrate the positive effect of low-concentration isovalent-cation substitution on the insertion characteristic of slowly diffusing multivalent ions. Inspection of the CV curves in Figure 4(a) reveals that the dominant feature in all cases is the appearance of the current spike associated with the sluggish transport of Mg-species across the electrode-electrolyte interface, similar to the pure KHTB phase. However, ionic substitution in W site clearly improves the overall kinetics of Mg^{2+} insertion. Figure 4(b) shows the CV curves for Zn²⁺ insertion into pure and substituted KHTB samples. A simple comparison with Mg²⁺ insertion reveals two major differences. First, the insertion of Zn²⁺ into the host is more facile compared to that of Mg²⁺. Indeed, for Zn²⁺, the kinetics of Zn/Zn²⁺ electrodissolution on the anode is fast enough so that the diffusion-controlled current is visible on the cathode (i.e. a current peak or step). Second, the insertion potential of Zn in KHTB has shifted to a much lower potential compared to Mg²⁺ insertion, due to the less negative potential of Zn^{2+}/Zn . In this regard, the reduction current is significant at potentials below 0.5 V vs Zn^{2+}/Zn , whereas for the magnesium cell, cathodic current flows once the potential drops below 1.5 V vs Mg²⁺/Mg. Also, confirmatory tests have been performed to prove that during the electrochemical cycling, the current is due to reversible insertion/extraction of Zn2+ and not the residual K+ (Figure S₇).



Figure 3 (a) Cyclic voltammetry curves of Mg-ion insertion/extraction into/from KHTB host. SPEIS contour plots acquired during (b) the cathodic and (c) anodic directions in the Mg|KHTB cell; the impedance complex phase angle (ϕ) is plotted as the third dimension using the color spectrum. The potential scan direction is indicated in panels (b) and (c) with an arrow.



Figure 4. Cyclic voltammetry curves for Mg (a) and Zn (b) insertion/extraction in pure and substituted KHTB phases.

The insertion voltages of Mg^{2+} and Zn^{2+} ions in KHTB with a nominal composition of $M_{o.125}K_{o.25}W_3O_9$ (M: Mg^{2+} , Zn^{2+}) have been estimated using DFT. The obtained insertion voltage for Mg^{2+} is 1.52 V, which is in line with the observed onset current according to the Figure 4(a). On the other hand, Zn^{2+} yields an insertion potential of 0.20 V, which is some 200 mV lower than the observed onset current (Figure 4(b)).

The results of the CV studies (Figure 4) clearly pinpoint the constructive effect of cationic substitution on the enhancement of the overall kinetics of the electrochemical insertion of the divalent Mg²⁺ and Zn²⁺ ions. This may be explained by considering the local distortion created by cation substitution that create microstrain in the crystal, leading to the cracking and significant particle size reduction (Figure S₅). Therefore, the added electrolyteelectrode contact area may results in a higher total current. It is worth noting that such level of microstructure modification has achieved with a low-level introduction of Cr and Mo dopants.

Following the demonstration of the redox activity of Mg^{2+} and Zn^{2+} ion insertion into KHTB, galvanostatic tests were attempted with an aim to extract the voltage-

composition relationships as well as the maximum charge storage capacity in the bronze phases. Even though Mg²⁺ can be inserted/extracted into/from KHTB phases under controlled-potential conditions (CV), it was realized that a constant current insertion attempt fails to insert significant amounts of Mg2+. This is a direct consequence of the very slow charge transfer at the electrodeelectrolyte interface, which prohibits maintaining a constant flux of Mg²⁺ species across the phase boundary. As a result, negligible degree of Mg²⁺ insertion was observed, equivalent to $Mg_{0.02}K_{0.25}W_{3}O_{9}$ (C/350)rate), $Mg_{0.06}K_{0.25}(W_{0.90}Mo_{0.10})_{3}O_{9}$ (C/100 rate), and $Mg_{0.06}K_{0.25}(W_{0.95}Cr_{0.05})_{3}O_{9}$ (C/100 rate) for the pure and cation-substituted cathodes (Figure S8(a)). On the contrary, potentiostatic insertion and extraction at the maximum thermodynamic driving force ($E_c = 0.1 \text{ V vs.}$ Mg^{2+}/Mg , $E_a = 2.0 V vs$. Mg^{2+}/Mg) yields nominal compositions of Mg_{0.07}K_{0.25}W₃O₉, Mg_{0.18}K_{0.25}(W_{0.90}Mo_{0.10})₃O₉, and Mg_{0.14}K_{0.25}(W_{0.95}Cr_{0.05})₃O₉, indicating significantly higher amounts of Mg²⁺ insertion into the cation-substituted cathodes at large overpotentials (Figure S8(b)). Unlike the magnesium systems, galvanostatic cycling shows higher amounts of Zn²⁺ insertion, with first-cycle capacities of up to $Zn_{0.02}W_3O_9$, $Zn_{0.08}K_{0.25}(W_{0.90}Mo_{0.10})_3O_9$, and $Zn_{0.11}K_{0.25}(W_{0.05}Cr_{0.05})_{3}O_{9}$ at a higher rate of C/50 (Figure S8(c)). Furthermore, deep-discharging of Zn cells at 10 mV vs Zn²⁺/Zn allows insertion of 0.2 moles of Zn (0.4 electron transfer) per W_3O_9 formula unit (Figure S7). The amount of Mg²⁺ insertion into the hexagonal tungsten trioxide achieved here is considerably lower than what has been reported previously for the monoclinic analog (0.32 Mg²⁺ per WO₃).³⁶ Therefore, it is possible that this discrepancy originates from the structural differences between the two polymorphs of WO₃.

Apart from the cooperative effect of cationic substitution on the divalent-ion insertion kinetics, it is of particular interest to compare the bulk diffusivities of Mg²⁺ and Zn²⁺ ions within the same host. Based on the CV studies, our findings suggest that the magnesium organohaloaluminate electrolytes mask the observation of Mg2+ diffusion in KHTB cathode. As a workaround, two supplementary studies has been designed to study the pure diffusivities of the divalent ions in the KHTB host, independent from the antagonistic anode/electrolyte interferences of the Mg-system. In the first approach, symmetric cells using KHTB phases were assembled and the bulk diffusion of the divalent ions was studied through EIS. For these tests, initially the KHTB cathodes were reduced in fullcells against Mg and Zn anodes, followed by extraction and washing off the electrolyte and assembling of the symmetric cells. To avoid complications arising from the organohaloaluminate-based electrolytes, $Mg(ClO_4)_2$ in acetonitrile, a conventional simple salt electrolyte, was used for Mg-containing systems. Typical EIS curves resulting from symmetric cells plotted in Bode representation are shown in Figure 5, with the fitting results presented in Table S1 and Figure S9.

In order to minimize the problems associated with the correlation and arbitrariness instigated by complicated EIS models, a minimal equivalent circuit comprising three parallel configurations of R|C elements arranged in series was adopted for fitting purposes, which adequately addresses the problem. The three R|C components in the order of decreasing frequency represent, respectively, solid-electrolyte interface impedance, charge transfer resistance, and ionic diffusion resistance. The diffusion resistances obtained yield 1.14 × 10⁶ and 1.18 × 10⁵ Ω , respectively, for Mg²⁺ and Zn²⁺. This clearly indicates that given all other experimental variables are kept constant, the Mg²⁺ solid-state bulk diffusion resistance is an order of magnitude larger compared to that of Zn²⁺ ion in the KHTB host.



Figure 5. Nyquist impedance responses of symmetric Znand Mg-inserted KHTB electrodes. The acquired data points and fit results are shown with respectively, open circles and lines. The inset shows the Bode phase representation and the quality of the fits over the employed frequency range.

For the second study, a new chronopotentiostatic experiment has been designed, which indirectly measures the relative diffusion rates of the divalent ions in KHTB host. The method works based on the measurement of the decay rate of the strong oxidizer, MnO_4^- from an aqueous solution, due to the reduction by the discharged $M_x K_{0.25}(W_{0.95}Cr_{0.05})_3O_9$ (M: Mg, Zn) electrodes. Note that due to the stability of the KHTB phase in even strongest acidic solutions, no dissolution was observed. Also, the relatively high redox potential of the tungsten in the reduced KHTB relative to the H⁺/H₂ couple allows it to be stable in the acidic solution (i.e., no oxidation by H⁺ is evident).

Figure 6 shows the Chronopotentiometric curves of the permanganate solution at various states. The permanganate decays very slowly in an acidic solution (red trace curve). Also, the PVDF-carbon mix does not alter the rate

of MnO_4^- decay (blue trace), as is the case with charged $K_{0.25}(W_{0.95}Cr_{0.05})_3O_9$ electrode (cyan trace). In the presence of reduced KHTB electrode, the potential of the solution rapidly drops, due to the chemical oxidation of the reduced M-KHTB (M: Mg, Zn) by the MnO₄⁻ oxidizer. As the reduction of MnO₄⁻ occurs exclusively on the surface of the KHTB crystals, the overall reduction rate (and hence the decay rate) of the MnO₄⁻ species is limited by the diffusion of the Mg²⁺ and Zn²⁺ ions from the bulk of the KHTB phase to the surface. From Figure 6, it is evident that the rate of the potential decrease is considerably faster for Zn-KHTB (purple trace) compared to Mg-KHTB (green trace); therefore, it is obvious that under identical conditions, and independent from any electrolyte/anode contributions, pure Zn²⁺ diffusion in KHTB phase is significantly faster than the Mg²⁺ counterpart.



Figure 6. Chronopotentiometric permanganate decay rate measurements (initial normality: c.a. 0.33 mN). All measurements carried out at the room temperature under Ar purge and constant stirring.

The results of the EIS and the chronopotentiometric permanganate decay rate provide evidences for the faster diffusion kinetics of the Zn^{2+} ion in KHTB compared to the Mg²⁺ ion. Such an obvious difference in the mass transport properties of Mg²⁺ and Zn²⁺ points to basic chemical differences in their respective intercalant-host interactions. This is somehow unexpected given that Mg²⁺ and Zn²⁺ are often considered to be similar from a classical crystal chemistry point of view (*i.e.*, dipositive charge, crystal radii: Mg²⁺_{CN:6} = 0.86 Å, Zn²⁺_{CN:6} = 0.88 Å).⁵³

In order to unravel the underlying reason behind the contrasting diffusion behavior of Mg²⁺ and Zn²⁺ ions in the tungsten bronze environment, ionic diffusion paths and their related activation energies were probed in detail using the DFT based CI-NEB method. For this, the crystallographic insertion sites for each intercalant is needed as an input; however, K⁺ insertion site (position

2b) cannot be taken as a default for the cases of Mg²⁺ and Zn²⁺ insertion. Therefore, a Zn-inserted sample was prepared by reducing the Cr-substituted KHTB electrode to a final composition Zn_{0.2}K_{0.25}(W_{0.95}Cr_{0.05})₃O₉ (Figure $S_7(a)$). Subsequently the electrode was investigated by XRD analysis for locating the Zn²⁺ insertion site(s) (The XRD powder patterns of the KHTB electrode before and after Zn and Mg insertion is provided in Figure S10). This was performed by a combined Rietveld and Pawley refinement and creating the Fourier difference map (F_o-F_c) obtained by comparing the structure factors of Zn-inserted sample (i.e. the observed intensities) and Zn-deficient KHTB crystal model (i.e. the calculated intensities), as presented in Figure 7(a). The difference map reveals regions of high electron density within the unit cell corresponding to the missing Zn²⁺ scatterers, located at the center of the trigonal channels (4d sites). Figure 7(b) depicts the atomic environment of the Zn²⁺ cation within the KHTB host, while Figure 7(c) exhibits the Rietveld refinement of the XRD pattern of the Zn²⁺-inserted sample, with the Zn sites included in the model.



Figure 7. (a) Fourier difference map contour plot of the Zninserted KHTB as viewed along [oo1] (z = 0.00 Å). The bright shade represents the possible locations for the Zn atoms. (b) The 9-coordinated atomic environment of Zn within the KHTB crystal at site 4d. (c) Rietveld refinement of Zn_{0.2}K_{0.29}W₃O₉ including the Zn atoms in the crystal model. For (c), the Zn and K site occupancies have been obtained by refinement.

The occupation of 4d sites by Zn^{2+} and the results of the unusual tricapped trigonal prismatic coordination of Zn center (Figure 7(b)) may be understood by considering two arguments: (1) mild electrochemical Zn^{2+} insertion

into KHTB allows metastable configurations, and (2) a better fulfillment of bond valence sum (BVS) makes occupation of 4d sites by Zn^{2+} preferable (Zn BVS = 1.73 and 1.22 for 4d and 2b sites, respectively). Previously, it has been reported that the HTB structure can be electrochemically intercalated with Li⁺ ions, surpassing its site 2b full occupation limit (one Li⁺ per W₃O₉ unit).³⁰ This, along with the conservation of the XRD pattern of the "over-lithiated" sample suggests that extra insertion sites, such as 4d, would be actively accommodating the inserted ions. Additionally, due to the similarity of the ionic and crystallographic sizes of Mg²⁺ and Zn²⁺, an insertion site for Mg²⁺ that is similar to that of Zn²⁺ has been assumed, which has been further verified via DFT (*vide infra*).

In the context of the multivalent-ion hosts, the conversion reaction is a major competitor for the topotactic insertion reaction reported previously through experimental and comprehensive theoretical studies. 54-56 However, Regarding the current case, we have not observed any evidence to consider the occurrence of a conversion reaction after the electrochemical insertion of Zn²⁺ and Mg²⁺ into the KHTB phase. One reason could be that the room-temperature electrochemical (de)insertion is often considered a soft-chemistry method, which may yield products that may be considered metastable from a thermodynamic point of view. Furthermore, inspection of the XRD patterns before and after the insertion of Zn²⁺ (Figure 7, Figure S10, and Table S2) exhibits the intensity mismatch and slight lattice volume expansion due to the insertion of the guest ions (heavy lattice strain can be observed due to Mg insertion). Finally, in the case of Zn²⁺ ions, we can observe that electrochemical cycling yields a small, but reversible capacity with a coulombic efficiency of > 95% (Figure S8(a)). Since the conversion reactions are highly irreversible (due to the difficulty in the decomposition of MgO and ZnO products), the observed charge transfers should originate from reversible and topotactic insertion reactions. Therefore, the results obtained here support a topotactic intercalation of the divalent cations into the KHTB structure.

The fact that the XRD pattern of the Zn-reduced KHTB phase can be indexed and refined using the same crystal model as the starting material indicates that the reduction of the host follows a topotactic cation insertion pathway, and thus the possibility of a conversion reaction has been ruled out. Furthermore, the sloppy nature of the voltage profiles (Figure S8(a,c)) suggests that the topotactic transformation is indeed a single-phase, solid-solution type reaction, where the insertion potential varies with the composition.

With the insertion sites located, diffusion paths for the divalent ions have been initialized by assuming an ionic hop from the center of the trigonal channel to the center of the hexagonal channel (path $4d \rightarrow 2b$) and another one connecting the 2b sites along the center of the hexagonal

channels, assuming no blockage by K⁺ ions. The schematics of all relevant site positions and the diffusion paths for the divalent ions are represented in Figure 8. The procedure for distributing K⁺ ions at sites 2b is elaborated in the SI. Feeding these initial paths into DFT-NEB engine yielded a metastable site, namely position 12i, ruling out 2b and 2a as stable sites for Mg²⁺ and Zn²⁺ diffusion (Figure 9(a)).

Figure 8 exhibits the optimized diffusion path for Mg²⁺ and Zn²⁺ ions in the KHTB lattice. The diffusion in each case starts from the global minimum in the potential energy surface (PES) (site 4d). Figure 9(a) provides the DFT derived site-specific energies; as evident, the variation of relative energy with site is much larger for Mg²⁺ as compared to Zn²⁺, suggesting Mg²⁺ is very sensitive towards the choice of site occupation. It can be inferred from such a large energy difference that at low to moderate temperatures, Mg²⁺ exclusively occupies the 4d sites, whereas Zn²⁺ may occupy both the 4d and 12i sites following a Boltzmann distribution ($\Delta E_{4d-12i} = 0.025 \text{ eV}, \text{ kT} = 0.0257$ eV @ 298 K). Therefore, for the Zn²⁺ cation, the ionic jumps between successive 12i sites forms a minimum energy diffusion path. This, along with the activation energies for ionic diffusions (Figure 8(c)) explains the rather facile ionic diffusion of Zn²⁺ in KHTB lattice compared to that of Mg²⁺. For the latter, a complete jump between two 4d sites requires surpassing two transition states with activation energies exceeding o.8 eV, leaving Mg2+ effectively trapped in the 4d site.



Figure 8. Depiction of the initial (yellow) and optimized path for Zn^{2+} (green) and Mg^{2+} (orange) ions, as viewed along the length of the 1-D channels (a), and $[\overline{110}]$ (b). Pertinent Wyckoff sites are marked. The transition-states for Mg^{2+} (Zn^{2+}) is indicated with red (blue) spheres (further refer to

Figure 9). Panel (c) shows the pseudo-square planar coordination of the diffusing ions at the 4d-12i path transition-state (purple diamonds).

On the contrary, while diffusion of Zn^{2+} between 4d and 12i is inhibited by a large energy barrier (0.7 eV), diffusion among 12i sites only requires an activation barrier of 0.38 eV. This effectively reduces the activation energy associated with Zn-ion diffusion to half of that for the Mg²⁺ ion, explaining the relative difficulty in electrochemical cycling of Mg in KHTB.

It should be emphasized that the diffusion path and activation energies were obtained here by assuming no blockage from the remaining K⁺ ions. Such an assumption may apparently facilitate the long-range diffusion of the multivalent ions, whereas in the actual case, the presence of K⁺ ions in the hexagonal channels effectively interrupts such long-range ionic transport. From a statistical point of view, a quarter of the K⁺ sites are occupied following a composition of $K_{0.25}W_3O_9$ for the empty host. Given the existence of different ionic types, complicated migration mechanisms, such as correlated diffusion of Mg^{2+}/K^+ or Zn^{2+}/K^+ might play a deterministic role on the overall diffusion of the multivalent ions. Therefore, further investigations would be necessary to ascertain the assumption that K⁺ ions will not block a considerable fraction of the diffusion channels or to probe any cooperative ionic diffusion mechanism.

In the case of blockage of the hexagonal channels by a K⁺ ion, a change in the diffusion mechanism of the multivalent ions should follow for a long-range ionic hop to occur. The ions at site 4d have access to three 12i sites due to the hexagonal symmetry of the lattice. Thus, a blockage of the 1-D hexagonal channel requires a lateral diffusion of the multivalent ions from site 4d to a non-blocked 12i channel (along the (100) plane). For Mg²⁺, this is still the minimum energy path, but for Zn²⁺, the modified path imposes an extra 0.3 eV in energy cost compared to the more favorable 12i-12i direct hop.

Finally, it is imperative to note that the overall topology of the diffusion path should be considered to assess whether a long-range ionic diffusion is possible when multiple short-range diffusion paths are available. As a stereotypical example, the Chevrel phase Mg₂Mo₆S₈ exhibits a 3-D ionic diffusion path comprised by two crystallographically distinct Mg2+ sites.57 The activation energy for the Mg1 intra-site diffusion is low, as is evident by the disordered nature of Mg²⁺ site occupancies and relatively large root-mean-square of atomic displacement (0.11 Å at room temperature (RT)) compared to the Mg²⁺-Mg²⁺ distance (1.11(8) Å).⁵⁸ However, at RT, the diffusion is limited to the isolated Mg1-Mg1 sites, leaving the Mg2+ ions effectively trapped in the solid. On the other hand, heating to 60 °C establishes ionic exchange paths between the Mg1-Mg2 sites that leads to a percolated diffusion path across the crystalline solid. Extending this argument to the KHTB, the low energy 12i-12i diffusion path will form a percolated diffusion channel for Zn²⁺ only if they are not interrupted by blocked channels. For a real case with blocked channels, an intermediate diffusivity between the shorter low-energy path (12i-H2i) and the longer high-energy path (4d-H2i-H2i-H2i) would be more likely."



Figure 9. (a) KHTB Site energy analysis for Mg^{2+} and Zn^{2+} ions. (b) A 2-D representation of the potential energy surface for Mg^{2+} and Zn^{2+} diffusion among crystallographic sites of KHTB. Data points filled in red and blue are defined as in Figure 8.

In order to gain a deeper understanding into the origins of activation energies for Zn²⁺ and Mg²⁺ diffusion in the KHTB structure, we selected the initial state of the ion-hopping path (site 4d) along with the two transition states for further analysis. In the context of ion diffusivity, KHTB is not the native and preferred lattice for storage of small divalent ions. Consequently, the inserted ions heavily lack their preferred coordination environments. The first transition-state (TS1) for both cations appears to originate from electrostatic repulsions induced by the passage of the divalent ion from a square-shaped 8-member ring, constructed by alternative arrangement of W and O atoms (highlighted in the polyhedral view of Figure 8(a) by red dotted line). Therefore, the narrow diameter of this opening (3.7 Å in edge) and close proximity of the divalent ion to the hexavalent W atoms, and repulsion of electronic clouds necessitates overcoming an activation energy as high as 0.70 and 0.84 eV, respectively, for Zn²⁺ and Mg²⁺ (Figure 8(c), 4d-12i region, blue- and red-filled data markers). The situation for the second transition state (TS2) along 12i→12i is different and roots in the dissimilar chemical nature of Mg²⁺ and Zn²⁺ ions. Being located within the large hexagonal channels, the divalent cations are extensively undercoordinated along the diffusion path. Table 1 lists the negated values of crystal orbital Hamilton population (COHP) along with the calculated Bader charge for magnesium- and zinc-ion at various sites. Briefly, COHP considers the strength of orbital overlap between a pair of atoms, such that a large negative value indicates a strong bonding interaction,

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whereas positive values indicate primarily anti-bonding interactions between the pair of atoms.

Table 1. Metal-oxygen Crystal Orbital Hamilton Population (COHP) along with Bader charge analyses of Mg and Zn atoms at various crystallographic sites within KHTB crystal.

	Cation	Cation position		
		4d	TS1	TS2
-COHP	Zn	8.3	7.7	3.3
	Mg	8.1	6.9	4.3
Bader charge	Zn	+1.28	+1.28	+0.86
	Mg	+1.98	+1.93	+1.97

From Table 1, evidently the strength of the bonding interactions between the inserted cations and the oxide anion falls significantly as the ions diffuse into the large hexagonal channel (at TS2), indicating the loss of coordination. Therefore, the magnitude of the activation energy for each ion is a direct function of how it can adapt to the destabilizing conditions of becoming undercoordinated. Figure 10 9 depicts the electron spin densities for the inserted ions at TS2 along the 12i→12i diffusion path. According to Table 1, regardless of its position within the lattice, Mg²⁺ ion maintains the divalent state. This is exemplified in Figure 109(a) by the non-magnetic state of the system and spin pairing at TS2, which is expected if a complete charge transfer from Mg 2s to the conduction band of KHTB occurs. In contrast, a snapshot of Zn-ion diffusion at TS₂ (Figure 10 9(b)) suggests that some electron transfer has occurred from the valence band of the KHTB host to the Zn cation so that the unpaired electron spin partially fills the 4s orbital of Zn, leaving back a hole in the valence band of KHTB that is mainly t_{2g} in character. This momentary inverse flow of electrons from the host to the guest is further evident by a decrease in the magnitude of the positive charge on the Zn-ion at TS2 compared to the 4d stable position (Table 1).

From a theoretical and practical points of view, this host-to-guest charge transfer may be explained based on the low insertion potential of Zn^{2+} in KHTB host (Figure 4(b)); this implies that the energy difference for the electron to occupy Zn-orbitals or KHTB bands is relatively small. The partial compensation of the dipositive charge of the zinc cation in an undercoordinated transition state lowers the activation energy of Zn-ion diffusion in contrast to the Mg²⁺ ion. This difference in behavior is purely chemical in nature, reflecting the higher electronegativity of Zn and its tendency toward covalent bond formation, which is further confirmed by its Bader charge being consistently less positive than the +2 formal charge (Table 1). In fact, similar to Mg²⁺ ion, the occurrence of metastable monovalent Zn^+ ion is an established topic with several reports and reviews.^{59,60}



Figure 10. Electron spin-density map (projected along [001]) for (a) Mg-ion and (b) Zn-ion in the KHTB lattice at the second transition state along the 12i \rightarrow 12i ionic hop. The contour surface in each case was drawn at 2 × 10⁻³ μ B/Å³.

It is postulated and generally accepted⁶¹ that multielectron redox reactions follow through sequential elementary reactions (*i.e.*, single-electron transfers) with different rate constants. However, our knowledge of solid-state diffusion of multivalent ions and the corresponding mechanisms for charge redistribution is still very limited. Whether the rate-determining-step in multivalent ion diffusion may take an elementary form similar to monovalent ions (as demonstrated here for the specific case of Zn-ion) is a question that requires further investigation.

The results of this work suggest that for the given oxide-based host tested, Mg^{2+} diffusion is slower than Zn^{2+} due to the fundamental chemical differences and the iono-covalency arguments of M^{2+} —O bonds. However, generalization of such conclusion to all oxide materials requires detailed experimental and theoretical studies on other host materials. If such conclusions are valid, this can impose consequences on divalent cells. Even though Mg has a reasonably low redox potential (-2.34 vs SHE), a slower diffusion kinetic necessitates extensive downsizing and crystal engineering. On the other hand, faster diffusing Zn^{2+} has a much positive redox potential, which reduces the cell voltage.

Despite the fact that ionic diffusion is a strong function of the crystal structure and local environment of the diffusing species, the results of this work show that certain effects may originate from the differences in the chemical nature of Mg^{2+} and Zn^{2+} ions. Therefore, it suggests that due to the stronger ionic interactions, Mg^{2+} diffusion in oxidic hosts may suffer from slow kinetics in comparison to the Zn^{2+} counterpart. Verification of such claims requires fundamental studies of Mg^{2+} and Zn^{2+} diffusion in other systems, which is the subject of our ongoing research.

CONCLUSIONS

The pure and isovalent-cation-substituted variants of the potassiated form of the hexagonal tungsten bronze have been synthesized and assessed in Mg-ion and Zn-

ion full-cells for evaluation of the basic differences in the mass transport of divalent Mg2+ and Zn2+ ions. For the cation-substituted phases, Mo and Cr have been substituted for the framework tungsten cations, respectively, by 0.1 and 0.05 mole fractions. The results from cyclic voltammetry tests show that the rate of Mg insertion/extraction in various KHTB phases is always limited by a slow electro-adsorption/desolvation of Mg-containing species at the electrolyte-electrode interface, and hence no solidstate bulk diffusion behavior is detectable. On the other hand, Zn²⁺ demonstrates a rather facile electrochemically driven insertion/extraction at an average voltage of 0.35 V vs. Zn²⁺/Zn. For Both cations, introducing site disorder via a partial substitution of W with Mo or Cr cations results in a significant improvement in the insertion kinetics of the divalent ions. This has been attributed to the combined effect of particle size reduction through lattice strain and improved bulk diffusivities. Further experimental studies were conducted on the symmetric cells to elucidate the basic differences in net diffusivities of Mg²⁺ and Zn²⁺ ions, with the results suggesting that Zn²⁺ diffusion in KHTB host is favored over that of Mg²⁺ ion. In an attempt to uncover this observation, the problem of ionic diffusion of the divalent ions has been treated theoretically at the DFT level. The outcomes suggest that the basic difference roots in the higher tendency of Zn²⁺ toward the formation of more covalent bond with the host oxide anions compared to the more electropositive Mg²⁺, thereby stabilizing the undercoordinated transition state by a momentary electronic charge flow from the host to the diffusing ion. Based on the results, it is expected that on a broader perspective, diffusion of multivalent ions in solid hosts to be considerably more complicated than for the monovalent counterparts; this is due to the variation in the iono-covalency of host-guest interactions as well as the possibility of unusual and metastable oxidation states on the multivalent ions.

ASSOCIATED CONTENT

Supporting Information. Additional EDS X-ray analyses of pristine and chemically oxidized, pure, and cation-substituted KHTB phases along with their digital photographs, SEM micrographs of the pristine samples, CV tests on blank cells, voltage-composition curves for electrochemically inserted Mg²⁺ and Zn²⁺ in KHTB phases and additional plots and tabulated data of the EIS fittings, and input structure selection for DFT calculations are provided as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported by the National Science Foundation grant DMR 1709081 and Welch Foundation grant F-1254. The authors also acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin for providing HPC resources that have contributed to the research results reported within this paper. URL: http://www.tacc.utexas.edu.

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