New Insight on the Unusually High Ionic Mobility in Chevrel Phases
E. Levi, G. Gershinsky, D. Aurbach, O. Isnard, and G. Ceder

Chem. Mater., 2009, 21 (7), 1390-1399 • DOI: 10.1021/cm900033v • Publication Date (Web): 13 March 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
New Insight on the Unusually High Ionic Mobility in Chevrel Phases

E. Levi,*† G. Gershinsky,‡ D. Aurbach,† O. Isnard,‡,§ and G. Ceder**

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel 52900, Institut Néel, CNRS, associé à l’Université de Grenoble J. Fourier, BP166X, 38042 Grenoble cédex 9, France, Institut Laue Langevin, BP 156 X, 38042 Grenoble cédex 9, France, and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received January 6, 2009. Revised Manuscript Received February 16, 2009

Chevrel Phases (CPs), M,MnO6T8 (M = metal, T = S, Se) are unique materials, which allow for a fast and reversible insertion of various cations at RT. Earlier, CPs were divided into two major types: type I with large immobile cations, which block any ionic transport in the diffusion channels, and type II with small mobile cations. Our analysis of available experimental data shows that the transport behavior in CPs cannot be understood in the framework of the blocking concept; it is much more complex and includes: (i) apparent immobility of the large M cations like Pb2+, Sn2+, Ag+ in the ternary phases, M,MnO6T8; (ii) coupled M + M’ diffusion in the quaternary phases, M,MnO6T8, where both large and small cations can assist; (iii) cation trapping in the Mg–MnO6S8, Cd–MnO6S8, and Na–MnO6T8 systems; (iv) a combination of low and high rate diffusion kinetics at the first and last intercalation stages, respectively, for the Cu–MnO6S8, Mn–MnO6S8, and Cd–MnO6S8 systems; and (v) a fast ionic transport for small cations like Ni2+, Zn2+, and Li+. A general structural approach (analysis of the polyhedral linkage in the diffusion channels of CPs and mapping of all the cation sites combined with their bond valence sum values and the distances from the adjacent Mo atoms) used for the first time for a variety of CPs shows two competing diffusion pathways of inserted ions for most of CPs: circular motion within the same cavity between the MoO6T8 blocks with activation energy Ec, and progressive diffusion from one cavity to the adjacent one with activation energy E with the character of the ionic transport depends mostly on the distribution of the repulsive forces for the inserted cations, as well as on the Ec/E ratio, affected in turn by the cation position, its size, cation–Mo interactions, and the anion nature.

Introduction

There is no question that rechargeable Li (ion) batteries are recently the leader in the market of high-energy-density power sources, but their safety and cost limitations stimulate the search for more systems for energy storage and conversion based on other active metals such as magnesium, aluminum, and zinc. One of the major problems of such systems is slow transport of the respective ions in inorganic hosts that can serve as cathodes for such batteries. Until now, only one family of materials, namely Chevrel phases (CPs), M,MnO6T8 (M = metal, T = S, Se), is known to allow for a fast and reversible insertion of various cations, monovalent (Li+, Na+, Cu+) as well as divalent: Zn2+, Cd2+, Ni2+, Mn2+, Co2+, Fe2+, and Mg2+ at ambient temperatures,1–9 which is associated with high electronic conductivity of the intercalation compounds.

Amazingly, these compounds can undergo insertion–displacement reactions as well, in which the insertion of one type of cations, Mn+ = Li+, Na+, Mg+, or Zn2+, in CPs may be accompanied by extraction of another cation, M'n+ = Na+, Cu+, Ag+, Ni2+, In+, Fe2+, or Co2+ (which exists in the pristine material) and its reduction, leading to the formation of metallic clusters as the reaction product3,4,16,17

\[
xM^{n+} + M'\gamma \text{Mo}_6\text{T}_8 + 4e^- = M\gamma \text{Mo}_6\text{T}_8 + yM'(\text{metal})
\]

(1)

Here the reaction suggests a coupled M–M' cations’ motion in the crystal structure of the quaternary compounds.

* Corresponding author. E-mail: elenal@mail.biu.ac.il.
† Bar-Ilan University.
‡ Institut Néel.
§ Institut Laue Langevin.
** Massachusetts Institute of Technology.
Mg batteries\textsuperscript{14,18,19} increased our interest in studying cations; it was assumed\textsuperscript{20,21} that the rhombohedral symmetry of CPs is limited by four electrons per Mo\textsubscript{6}\textsubscript{T}\textsubscript{8} clusters. Recent application of Mo\textsubscript{6}T\textsubscript{8} as unique cathodes for rechargeable Mg batteries\textsuperscript{14,18,19} increased our interest in studying cation mobility in CPs. For further development of new electrode materials for rechargeable Mg batteries, it seems very important first to understand in detail the interesting transport phenomena related to CPs. It is necessary to revise our knowledge about the diffusion processes in these unique compounds.

In spite of variation in symmetry (triclinic or rhombohedral), the crystal structure of all CPs is basically the same: a stacking of Mo\textsubscript{6}T\textsubscript{8} blocks (or Mo\textsubscript{6}-octahedral clusters inside anion cubes) with a system of open three-dimensional channels formed by face-sharing pseudocubic cavities 1 and 2 available for cation insertion (a strong repulsion between the Mo atoms and inserting cations does not allow the occupation of cavity 3) (Figure 1).\textsuperscript{20,22} In earlier studies,\textsuperscript{3,5} the unusually high mobility of small divalent cations in CPs was explained by quasi-monovalent state of these cations as transients, which results from a rapid one-electron transfer via the Mo\textsubscript{6}T\textsubscript{8} matrix, e.g., $\text{Zn}^{2+} + e^{-} \leftrightarrow \text{Zn}^+$. In addition, it was assumed\textsuperscript{20,21} that the rhombohedral symmetry of CPs with small cations (radius $< 1$ Å) is associated with a cation motion between equivalent sites, whereas the atomic “freezing” in one of the sites at a certain critical temperature is responsible for the triclinic distortion. Previously,\textsuperscript{26} we presented alternative explanation for a high mobility of multivalent cations in CPs, which was ascribed to a fast and efficient attainment of local electroneutrality by the octahedral Mo\textsubscript{6} clusters. It was also shown\textsuperscript{24} that there is no direct correlation between the CPs symmetry and the cation mobility. This paper is devoted to the effect of the cation nature on its diffusivity in CPs.

In general, cation transport in all CPs proceeds via vacant sites in cavities 1 and 2, but the environment and the arrangement of these sites inside the cavities differ surprisingly for different compositions.\textsuperscript{20–25} According to the cation position in the crystal structure and its ionic mobility, all the M\textsubscript{2}Mo\textsubscript{6}T\textsubscript{8} compounds were divided earlier\textsuperscript{1,20,21} into two major groups: type I with constant $x = 1$ and large (radius $> 1$ Å) immobile cations located exactly in (or very close to) the origin of cavity 1 (Figure 1), and type II with highly mobile, small (radius $< 1$ Å) ions shifted (“delocalized”) from the origin, where $x$ is limited by four electrons per Mo\textsubscript{6} cluster. In the latter case, the arrangement of the cation sites was described as inner (six equivalent tetrahedral sites in cavity 1) and outer (six equivalent tetrahedral sites located in six adjacent cavities 2) rings. It was also shown\textsuperscript{20,21} that the value of the cation delocalization depends mostly on the cation size: the smaller the cation, the higher is its shift from the origin of cavity 1. Thus, it was commonly accepted that the main parameter, which affects the cation mobility in CPs, is its size. However, the reason of the completely different mobility of large and small cations in CPs was not discussed in detail. It was only mentioned that large cations fall into a combined energetic/steric trap and block any ionic transport.\textsuperscript{3–5}

In fact, cavity 1, located on the intersection of the diffusion channels, provides only one site for large cations (in its origin or very close to the origin); thereby, its occupation by immobile ion should stop any ionic motion.

This suggestion agrees well with most of the synthetic results, which showed that CPs of group I could be obtained only at high temperatures, in contrast to CPs of group II, which can be produced by chemical or electrochemical reversible reactions as well at ambient temperatures. However, our analysis of available experimental data\textsuperscript{13–11,12,20–22,28–37}
(Tables 1 and 2) demonstrates that the ion-transport behavior in CPs is much more complex; it includes (i) apparent immobility of the large M cations like Pb$^{2+}$, Sn$^{2+}$, Ag$^+$ in the ternary phases, MMO$_6$T$_8$; (ii) coupled $M + M'$ diffusion in the quaternary phases, M$_x$M'$_y$Mo$_6$T$_8$, where both large and small cations can assist; (iii) cation trapping in the Mg$-$Mo$_6$S$_8$, Cd$-$Mo$_6$S$_8$, and Na$-$Mo$_6$T$_8$ systems; (iv) a combination of low and high rate diffusion kinetics at the first and last intercalation stages, respectively, for the Cu$-$Mo$_6$S$_8$, Mn$-$Mo$_6$S$_8$, and Cd$-$Mo$_6$S$_8$ systems; and (v) a fast ionic transport for small cations like Ni$^{2+}$, Zn$^{2+}$, and Li$^+$. Thus, contrary to general expectation, there is no unambiguous correlation between the cation mobility and its size. Moreover, it is not clear how large cations “blocked” in MMO$_6$T$_8$ can move in the same crystal structure upon coupled $M + M'$ diffusion (more detailed discussion of the data is presented in the Supporting Information).

It should be mentioned that in the earlier publications, the above experimental results were neither systemized nor defined as typical for the CPs groups. For instance, a partial cation trapping was not recognized for the Cd$-$Mo$_6$S$_8$ system. Actually, the first stage of Cd insertion was presented as fully reversible electrochemical reaction at RT

$$\text{Cd}^{2+} + 2e^- + \text{Mo}_6\text{S}_8 \leftrightarrow \text{CdMo}_6\text{S}_8$$ \ (2)$$

whereas the formation of Cd$_3$Mo$_6$S$_8$ was described as a difficult process, which occurs very slowly. Furthermore, ref 5 states that the maximal intercalation level that can be reached for Cd$_x$Mo$_6$S$_8$ by an electrochemical insertion is $x = 1$. However, the evolution of the electrochemical response for the Cd$_x$Mo$_6$S$_{6-y}$Se$_y$ ($y = 0, 4, 6,$ and 8) series with characteristic potentials of Cd insertion, which was presented in ref 9, as well as its similarity with the data for the Mg$-$Mo$_6$T$_8$ system allow us to suggest the opposite interpretation of these experimental results: The fast reversible reaction discovered for Cd$_x$Mo$_6$S$_8$ should be referred to the second insertion stage ($1 < x < 2$). Moreover, reaction 2 is irreversible even at elevated temperature ($60\, ^\circ\text{C}$) because of the trapping of Cd$^{2+}$ cations in CdMo$_6$S$_8$, whereas substitution of sulfur atoms by selenium results in the fully reversible Cd$^{2+}$ ions insertion (at 60 °C). Thus, we believe that the transport behavior of Cd$^{2+}$ cations in CPs agrees well with the scheme presented above (see more detailed discussion in the Supporting Information).

Another important example is the problematic interpretation of the trapping phenomena in the Na$-$Mo$_6$T$_8$ systems, which allow for the insertion of four sodium cations per formula unit but subsequent extraction of only three of them. According to the authors, the insertion/deinsertion process is asymmetric: The first phase, which forms upon the electrode reduction, is Na$_3$Mo$_6$T$_8$, with high ionic mobility (type II of CPs), whereas NaMo$_6$T$_8$ (type I of CPs) can be obtained only upon the cation extraction:

$$\text{Na}_3\text{Mo}_6\text{T}_8 \leftrightarrow \text{Na}_2\text{Mo}_6\text{T}_8 + \text{Na}^+$$

$$\text{Na}_2\text{Mo}_6\text{T}_8 \leftrightarrow \text{NaMo}_6\text{T}_8 + \text{Na}^+$$

$$\text{NaMo}_6\text{T}_8 \leftrightarrow \text{Mo}_6\text{T}_8 + \text{Na}^+$$

$$\text{Mo}_6\text{T}_8 \leftrightarrow \text{Mo}_6\text{S}_8 + \text{S}^2-$$

$$\text{Mo}_6\text{S}_8 \leftrightarrow \text{Mo}_6\text{Se}_8 + \text{Se}^2-$$

$$\text{Mo}_6\text{Se}_8 \leftrightarrow \text{Mo}_6\text{Sey} + \text{S}^2-$$

$$\text{Mo}_6\text{Sey} \leftrightarrow \text{Mo}_6\text{Se}_{y-2} + \text{S}^2-$$

$$\text{Mo}_6\text{Se}_{y-2} \leftrightarrow \text{Mo}_6\text{S}_{8-y} + \text{S}^2-$$

$$\text{Mo}_6\text{S}_{8-y} \leftrightarrow \text{Mo}_6\text{S}_8 + \text{S}_2^-$$

Table 1. Data Related to Mobility of Large Cations in CPs at RT

<table>
<thead>
<tr>
<th>Host</th>
<th>Electrode insertion</th>
<th>Electrochemical insertion</th>
<th>Diffusion coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMO$_6$T$_8$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$_6$S$_8$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$_6$Se$_8$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$_6$Sey$_2$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$_6$Sey$_4$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$_6$Sey$_6$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$_6$Sey$_8$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$<em>6$Sey$</em>{10}$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$<em>6$Sey$</em>{12}$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
<tr>
<td>MMO$<em>6$Sey$</em>{14}$</td>
<td>$\ell$</td>
<td>$\ell$</td>
<td>$\ell$</td>
</tr>
</tbody>
</table>

To explain the trapping, the blocking concept for NaMo$_6$T$_8$ was used.$^{4,5}$ However, in light of this concept, it is unclear how the immobile Na$^+$ ions in NaMo$_6$T$_8$ allow for further Na insertion and the formation of the intercalation compounds, Na$_x$Mo$_6$T$_8$, up to $x = 4$ at RT.

The unusual asymmetric mechanism of Na insertion was confirmed by phase analysis performed by in situ$^4$ and ex situ$^5$ X-ray diffraction (XRD). However, the researchers$^{4,5}$ presented contradictory conclusions about the symmetry of the Na$_x$Mo$_6$S$_8$ ($x = 3$ and 4) phases: They were found to be rhombohedral in the ex situ experiments and triclinic in the in situ one. Thus, it can be suggested that the in situ XRD patterns, obtained upon the first Na insertion for $x = 1$ and assigned by the authors$^4$ as a mixture of Mo$_6$S$_8$ and triclinic Na$_x$Mo$_6$S$_8$, should be related rather to a mixture of three rhombohedral phases, Mo$_6$S$_8$, Na$_x$Mo$_6$S$_8$, and Na$_3$Mo$_6$S$_8$ (a formation of such a mixture is quite possible because of nonequilibrium conditions caused by slow Na diffusion in Na$_x$Mo$_6$S$_8$ for $x < 1$). Hence, we believe that Na insertion into Mo$_6$T$_8$ follows the same major stages as Li insertion:$^{6}$ Mo$_6$T$_8$ $\rightarrow$ MMo$_6$T$_8$ $\rightarrow$ M$_2$Mo$_6$T$_8$ $\rightarrow$ M$_3$Mo$_6$T$_8$, $M = Na$ or Li, whereas the quite different electrochemical behavior of these systems (obvious Na trapping vs high Li mobility) should be related to the expected structural difference in the cation positions inside cavity 1 for the MMO$_6$T$_8$ compounds.

Actually, in our previous work devoted to Mg$^{2+}$−Mo$_6$T$_8$ systems,$^{25,26,35,37}$ we proposed an alternative trapping mechanism: The apparent partial immobility of Mg$^{2+}$ cations upon their extraction from MgMo$_6$S$_8$ at RT was explained by the specific features of the CPs crystal structure, namely by the ring arrangement of closely located vacant sites (inner ring) in cavity 1 with low potential energy. At low levels of Mg insertion into Mo$_6$S$_8$, i.e., upon formation of rhombohedral MgMo$_6$S$_8$, such an arrangement should result in a fast circular motion of the Mg$^{2+}$ ions within the same cavity 1, as well as in a high activation barrier for migration between different cavities. Progressive bulk diffusion becomes possible because of repulsion between inserting cations, i.e., it necessitates the presence of the second cation in the same group of sites (six inner plus six outer sites). As a result, the characteristic features of the system are the overvoltage upon reduction and trapping upon oxidation for $x < 1$, as well as a fast diffusion for $x > 1$ (note that the same features are typical for Na and Cd insertions). In the selenide host, a triclinic distortion caused by Mg insertion changes the geometry of the cation sites and leads to the high Mg mobility in the whole intercalation range ($0 < x < 2$).$^{25,26}$ Trapping can be prevented by using a ternary host, M$^{+}$,Mo$_6$T$_8$. For instance, full reversibility was attained upon Mg insertion into CuMo$_6$T$_8$, as the Cu−Mg repulsion in the cavities results in Mg detrapping.$^{16,17}$

The aim of the present article is to explain the peculiarities of the cation transport for the CPs variety by using the same structural approach as was applied previously for the separate Mg−Mo$_6$T$_8$ systems. For this, we analyzed the diffusion routes of different cations in the CPs’ crystal structure, especially in the CP compounds formed at the first stages of cation insertion (As was mentioned above, the ionic transport in the compounds with high intercalation level should be normally a priori fast because of cation−cation repulsion). According to the previous efforts in this area,$^{24,26}$ such analysis should be based on the mapping of all the cation sites and requires knowledge of exact crystal structures of the intercalation compounds. Thus, we used the available literature data and performed X-ray and neutron refinements for a number of unknown crystal structures (the experimental results we obtained in this work, devoted to the phase diagrams of several interesting M-Mo$_6$T$_8$ systems, will be presented in a separate paper). It should be noted that the CPs related to the present study were chosen according to the availability of information about the ionic mobility of cations in them.

### Structural Approach for Understanding Cations Diffusion in CPs

In general, in order to show the relation between structural and transport parameters of any ionic solid and to follow a possible cation pathway upon diffusion, it is necessary (i) to describe the crystal structure as a set of the linked polyhedra (in accordance to the first Pauling’s rule), (ii) to

| Table 2. Effect of the Cation Character and the Intercalation Level on the Diffusion Kinetics in CPs (case of “small” cations) at RT |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| cation          | cation radius   | exact crystal   | $x \leq 1$      | $x > 1$         | ref.            |
|                 | for CN = 6 (Å)  | data for M$_x$Mo$_6$T$_8$ | (or 2 for Cu$^+$) | (or 2 for Cu$^+$) | additional phenomena |
| Li$^+$          | 0.68            | Mo$_6$S$_8$     | R$_3$, classic type II$^{11}$ | fast            | fast            | 6, 7, 11, 30, 31 |
| Ni$^{2+}$       | 0.74            | Mo$_6$S$_8$     | R$_3$, classic type II$^{20,21}$ | fast            | fast            | 8, 11            |
| Zn$^{2+}$       | 0.83            | Mo$_6$S$_8$     | R$_3$, new type$^{20}$ | fast            | fast            | 5               |
| Cd$^{2+}$       | 0.99            | Mo$_6$S$_8$     | R$_3$, classic type II$^{20,21}$ | slow            | fast            | 13, 32           |
| Mn$^{2+}$       | 0.91            | Mo$_6$S$_8$     | R$_3$, new type$^{20}$ | slow            | fast            | 8               |
| Mg$^{2+}$       | 0.98            | Mo$_6$S$_8$     | P$_1$, new type$^{20}$ | fast            | fast            | slow trapping for $x < 1$ |
| Na$^+$          | 0.88            | Mo$_6$Se$_8$    | R$_3$, unknown | slow            | fast            | 5, 9, 10         |

The interpretation of the experimental data related to Cd$^{2+}$ insertion into Mo$_6$S$_8$ differs from that of ref 5, 9, and 10 (see text).
estimate the activation energy of hopping based on the anion and cation environments around each cation site involved in the diffusion, and (iii) to determine the distances of the cation hopping. In the past, such an approach was never fully applied for CPs. Description of the cation environments was restricted to “continuous transition between an eight-fold and a four-fold coordination” of cations in cavity 1, relative arrangement of the inner and outer sites (Figure 2a), or their schematic positions inside the cavities (Figure 2b). The maps of the cation sites presented for a few CPs include nothing more than dimensions of the inner and outer rings and their separation (Figure 2c).

The problem is that the simplified presentations accepted for CPs are insufficiently informative for the diffusion analysis. For instance, a fast diffusion in Ni₃Mo₆S₈ was explained by short separation between adjacent outer rings, i.e., a direct cation hopping between points 1 and 2 was assumed (Figure 2). However, according to the polyhedral structure of cavity 2 for such compounds, it is clear that the hopping between these sites is not direct, but should include an additional transport step in the neighboring tetrahedral interstitials (point 3 in Figure 2d). As a result, the distances between adjacent outer rings in CPs might be less important for the cation motion than the environment of the transport site (especially, the distance of the point 3 from Mo atom), because of a crucial influence of the latter on the activation energy of hopping. Thus, our first task in the diffusion analysis is to describe the polyhedral linkages in CPs, in order to determine the positions of all the cation sites (including the transport ones) in the centers of these polyhedra, their environment, and interconnections.

**Polyhedral Linkages in CPs.** The absence of polyhedral presentations for CPs can be explained by the versatility of their structural types. As a result, the polyhedral linkages inside the pseudocubic cavities 1 and 2, i.e., in the diffusion channels, may be quite different (Figures 3 and 4). In addition, it is not so simple to understand the position and the environment of possible transport sites, which remain vacant at all steady intercalation stages. To see the problem,

---

(CN = 5).

The distance between the Sn and Fe sites was found to be 2.14 Å, which is quite convenient for cation hopping. Note also that such a polyhedral linkage provides a window of four anions (the pyramids’ bases), which is much easier for cation jumping than that of three anions (tetrahedral faces).

Figure 4 illustrates the versatility of the sites’ environments in CPs with small cations, which was already discussed in our previous papers. In the CPs hosts, Mo₆S₈, and classic CPs with small cations, such as rhombohedral CuₓMo₆S₈, both the cavities 1 and 2 are composed of six tetrahedra, but differently linked to each other (Figures 2d and 4a). Another important example is the crystal structure of triclinic MnMo₆S₈, which nicely demonstrates the difference in the polyhedral polyhedra can be found in ref 22): (i) six tetrahedra in cavity 2–1 (Figure 4b); (ii) [MnS₈] octahedron linked to two empty tetrahedra in cavity 2–2 (Figure 4c), and (iii) a combination of two square-pyramids and two tetrahedra in cavity 2–3 (Figure 4d). Cavity 1 in MnMo₆S₈ has the same polyhedral structure as cavity 2–3 with a wide window of four anions between the cavities (this window may be considered as favorable for cation diffusion). On the basis of the knowledge of these polyhedral linkages, it is possible to go to the second stage of the diffusion analysis: to correlate the structural parameters of the cation sites to the energetic ones.

Mapping of the Cation Sites in CPs. In general, the crystal structure of an intercalation compound can be presented as a map of the equipotential levels, where, at different intercalation stages, the inserted cations occupy subsequently the wells with increasing potential energy. (Note that the potential energy surface will be modified as intercalation proceeds. Thus, it depends not only on the structure of the host but also on the multiple interactions between the ions of the host and the inserting cations.) The energy of sites can be predicted by ab initio calculations, but the inconsistent results obtained by two different groups for the Mg–Mo₆S₈ system show that the application of this method for CPs is not simple. Thus, before performing such calculations, it is quite desirable to understand the structural factors that affect the thermodynamics and kinetics of cation insertion.

In previous papers, we used special maps of all the sites (including the transport ones) in cavity 1 and in three adjacent cavities 2 (The latter are equivalent for rhombohedral CP crystals, but different for the triclinic ones.). Typical examples of such maps are presented in Figure 5 (Note that the structure of three additional cavities 2 linked to cavity 1 by common faces is not shown in the maps, but it is identical to that of the presented ones, and it can be obtained by inversion in cavity 1’s origin). Here the circles represent the cation sites in the CP’s crystal structure, whereas the numbers inside the circles are the bond valence sums (BVS) for these sites. The closer the BVS to the formal electrostatic charge of the cation in ionic compounds, the more suitable is the size of the anion polyhedron for the cation insertion. The occupied sites are marked by blue color, whereas light and dark gray colors are used to distinguish (according to the BVS values) between empty sites that are suitable and inconvenient for cation intercalation, respectively. Thick circle lines mark the positions that are too close to Mo atoms. All the direct lines connect the centers of the face-sharing polyhedra, i.e., they describe the lengths of possible cation jumps. The only exception is the line between the opposite inner sites, which shows the diameter of the inner ring. The red lines mark possible pathways of the cation motion (See the analysis below). The tables in the maps present the shortest distances between the cation sites Mᵢ and the Mo atoms. Thus, the maps provide information not only about hopping lengths, but also about energetic parameters of the separate jumps (such as potential energies of the cations sites and activation barriers) in the form of the BVS values for the sites and the Mᵢ–Mo distances (additional maps for a variety of CPs with known ionic mobility can be found in the Supporting Information).

Results and Discussion

Two Competing Pathways for Cation Motion in Most of CPs. Figure 5a presents the maps of the cation sites for the host, Mo₆S₈, with the BVS values calculated for Cu⁺ cations (This cation is chosen, because its insertion results in minimal geometric distortion of the initial host structure). According to the BVS and the Mᵢ–Mo distances, the relations between the potential energies of the sites, Eᵢ, should be the following: Eᵢ of the inner sites < Eᵢ of the outer sites < Eᵢ of the central sites of cavity 2 < Eᵢ of the peripheral sites. The structural data show for the sulfides and for a part of the selenides confirm these simple considerations: Cations in these compounds occupy first the interstitials in cavity 1, as the most distant from the Mo atoms, and then the outer sites in cavity 2. This order breaks down only for the CPs’ selenides of transition metals, where specific metal–metal interactions between the cations and the Mo atoms result in the occupation of the central sites in cavity 2.

As can be seen in Figure 5a, the crystal structure of the host provides two competing pathways for inserted cations: (i) a circular one between the inner sites, with activation energy Eᵢ; and (ii) a progressive diffusion from one cavity 1 (or 2) to the adjacent one, with activation energy Eᵢ. In the latter case, the ionic transport includes four separate jumps: two identical (between inner M₁ and outer M₂ sites) and two different (between outer M₂ and central M₃ sites in cavity 2), with maximal activation energies. The peripheral M₄ sites, as the closest to the Mo atoms in most of CPs, are usually not involved in the diffusion because of strong M–Mo repulsion. These two competing pathways exist also in the majority of the intercalation compounds, MₓMo₆T₈ (Figure 5b; see also the maps in the Supporting Information), whereas the absence of the circular way for cations located

exactly in the origin of cavity 1 (Figure 5e) can be regarded as the limiting case. Below, we present some general considerations concerning the mobility of different cations in CPs.

Factors Affecting the Cation Diffusivity in CPs. Hopping Distances. Figure 6 presents the distances of the separate jumps between the cation sites, M1–M2, M2–M3, and M3–M2 (see the pathway from one cavity 1 to the adjacent one in Figure 5a), and the total pathway lengths of the progressive diffusion, M1–M2–M3–M2–M1, in the CPs with different cations as a function of their sizes (or, more precisely, the lengths of the ideal chemical bonds “cation-anion”). The tendency is very clear: all the distances are longer for bigger cations. However, even for large cations like Pb, Na, Ag, or La, the maximal length of the separate jumps does not exceed 2.3 Å (For comparison, the distance between adjacent tetrahedral and octahedral sites in spinel, Li$_x$Mn$_2$O$_4$, known as a fast Li conductor, is close to 1.8 Å). Thus, the increase in the hopping lengths for the large cations cannot be the crucial parameter, which limits their mobility in CPs. Moreover, it can be shown (see the Supporting Information) that the potential energy of the square-pyramidal (CN = 5) sites in cavity 1 for CPs with large cations is relatively close to that of the central site. Thus, it is quite

Figure 5. Typical maps of the cation sites for the rhombohedral (R) CPs: (a) Mo$_6$S$_8$, (b) Ni$_x$Mo$_6$S$_8$, (c) CuMo$_6$S$_8$, (d) InMo$_6$S$_8$, (e) NaMo$_6$S$_8$, (f) LaMo$_6$S$_8$. The projections are normal to $-3$ symmetric axis. The inserts show the polyhedral structure of cavities 1 and 2 (the orientation of the polyhedra is not related to the translation vectors). The occupied sites are colored by blue.
possible that formation of such compounds as NaMo₆S₈ proceeds via an intermediate metastable step with shifted cation location and, respectively, lower hopping lengths for separate jumps.

Energetic Characteristics of the Cation Sites and $E_d/E_c$ Ratio. The most obvious characteristic feature of the maps for the MₓMo₆T₈ compounds ($x \approx 1$) is a well-known adaptation of cavity 1 to cation insertion (Figure 5b–f), which appears as (i) variations in the cation CN and (ii) almost linear correlations (for the rhombohedral phases) between the cation sizes, cations’ delocalization, and the $M_i$–Mo distances (Figure 7). As a result of lower delocalization and higher $M_i$–Mo distances, the potential energy of the sites in cavity 1 decreases for larger cations. In contrast, the geometry of cavity 2 at this intercalation level remains almost unchangeable: the $M_2$–Mo and $M_3$–Mo distances for CPs with different cations are very close. The sizes of the interstitials in cavity 2 are similar to those of the host and suitable only for insertion of small cations. This steric inconvenience or apparent suppression of the interstitials in cavity 2 can be estimated by a relative difference between the sites’ BVS values and the formal cation charge $V$: $(\text{BVS-}V)/V$ (Figure 8). As can be seen, the increase in the apparent suppression with cation size is more drastic for the central sites in cavity 2 than for the outer ones. A combination of the larger steric inconvenience and the shorter $M_i$–Mo distances for larger cations results in the higher potential energy for all the sites in cavity 2, but especially for the central ones.

It is clear that the diffusion activation energies depend not only on the atomic positions in the crystal structure, but also on the cation charge, as well as on the character of the $M$–Mo and $M$–T interactions. However, the BVS values and the $M_i$–Mo distances unambiguously testify: The larger are the inserted cations $M$, the higher is the difference between the potential energies of the sites in cavities 2 and 1, i.e., the larger are the activation energy of the progressive motion, $E_d$, whereas the bottleneck of the cation diffusion is

---

**Figure 6.** Distances of the separate jumps and the total pathway from one cavity 1 (2) to the adjacent one as a function of the lengths of the ideal chemical bonds “cation–anion”. The solid and dashed lines are related to the sulfides and selenides, respectively.

**Figure 7.** Correlations between the lengths of the ideal chemical bonds “cation–anion”, cations’ delocalization, and the $M_i$–Mo distances.
the central sites in cavity 2. The increase in $E_d$ should be accompanied by a decrease in the activation energy of the circular motion, $E_c$, because of the lower diameter of the inner ring (i.e., because of a combination of the shorter hopping distances and the lower potential energy for the inner sites). As a result, the circular motion becomes more favorable than the progressive one. These changes of the potential energy throughout the diffusion pathways for the CPs with different cation mobility can be illustrated in schematic relative way (Figure 9). Thus, the cation size itself has no pronounced effect on the ionic mobility of the intercalated species in CPs, but in most of the cases it determines the cation position in the crystal structure, and consequently, the $E_d/E_c$ ratio.

Repulsion between the Inserting Cations. The variation in the $E_d/E_c$ ratio explains well the difference in the ionic conductivity of large and small cations in CPs, but is still insufficient to clarify all the phenomena such as the insertion of large cations like Na$^+$ or K$^+$ at RT, the increase in the cation mobility for higher intercalation stages, and trapping or coupled diffusion with assistance of big cations. These phenomena can be understood only by taking into account the repulsion between the inserting cations as a driving force of the progressive diffusion (the latter can be roughly estimated by their metallic radius, i.e., the repulsion should decrease in the following sequence: K > Na > Pb > In > Mg > Sn > Cd > Li > Ag > Zn > Mn > Cu > Ni).

For small cations, such as Ni, Zn, and Li, their low repulsion is not so important, because the activation energies of the two competing diffusion pathways are low and very close: $E_d/E_c \approx 1$. As a result, these ions are highly mobile in the whole intercalation range (0 < $x$ < 2). For larger
cations, like Cu\(^+\) and Mn\(^{2+}\), the circular motion in their sulfides, MM\(_{\text{Mo6S8}}\), is energetically more attractive than the progressive one: \(E_d > E_c\). This results in relatively slow cation diffusion at the first intercalation stages \((x < 1)\). Only the cation repulsion upon insertion of the second or third cation (in the Cu\(^+\) case) per formula unit leads to the fast ionic transport (a similar mechanism can be proposed for the Cd\(^{2+}\) mobility in the Cd–Mo\(_6\)Se\(_8\) system).

An additional increase in the \(E_d/E_c\) ratio for the Mg–Mo\(_6\)S\(_8\), Cd–Mo\(_6\)S\(_8\), and Na–Mo\(_6\)T\(_8\) systems results in the phenomenon of partial cation trapping. It can be suggested that such big monovalent ions like K\(^+\) and Na\(^+\) can progressively move in the CPs structure only because of their high cation–cation repulsion. This suggestion agrees well with overvoltage typical for the Na electrochemical insertion and trapping upon its extraction. For large divalent cations, such as Sn\(^{2+}\) and Pb\(^{2+}\), \(E_d \gg E_c\), thereby their progressive diffusion in the microcrystalline Mo\(_6\)T\(_8\) is impossible. However, these cations can be inserted into the thin films. Moreover, trapped or “immobile” cations become mobile in the quaternary CPs upon coupled diffusion based on the presence of different cations in the same group of sites and their mutual repulsion. Thus, the CPs crystal structure is sufficiently flexible to provide progressive diffusion of large cations such as K\(^+\), Na\(^+\), Ag\(^+\), Sn\(^{2+}\), and Pb\(^{2+}\) in case where the pushing forces of the inserted cations (related to their mutual repulsion) are high enough to overcome the \(E_d\) energetic barriers.

Typical examples of more detailed diffusion analysis can be found in the Supporting Information.

### Conclusion

A general structural approach was used for the first time to explain the peculiarities of the cation transport in a variety of CPs at RT, such as: (i) immobility of large cations like Pb\(^{2+}\), Sn\(^{2+}\), Ag\(^{+}\) in the ternary phases, MM\(_{\text{Mo6T8}}\); (ii) coupled M + M\(^{+}\) cation diffusion, which can include the mass-transport of the large cations, in the quaternary phases, M\(_2\)M\(^{+}\)M\(_2\)T\(_8\); (iii) existence of partial cation trapping phenomena in the Mg–Mo\(_6\)S\(_8\), Cd–Mo\(_6\)S\(_8\), and Na–Mo\(_6\)T\(_8\) systems at RT; (iv) a combination of slow and fast diffusion kinetics at the first and last intercalation stages, respectively, for the Cu–Mo\(_6\)S\(_8\), Mn–Mo\(_6\)S\(_8\), and Cd–Mo\(_6\)Se\(_8\) systems; and (v) a fast ionic transport for small cations like Ni\(^{2+}\), Zn\(^{2+}\), and Li\(^+\). This approach includes: (i) analysis of the polyhedral linkages in the diffusion channels of CPs, which can be substantially different in the various CPs; (ii) mapping of all the cation sites combined with their BVS values and the distances from the adjacent Mo atoms. Such a combination allows us to not only know the hopping lengths but also estimate the energetic parameters of the separate jumps (potential energies of the cations sites and activation barriers).

The analysis shows two competing pathways for most CPs: circular motion between the inner sites with activation energy \(E_c\), and progressive diffusion with four separate jumps from one cavity 1 (or 2) to the adjacent one, with activation energy \(E_d\). Thus, the cation mobility in CPs at RT has three key contributions: two activation energies, \(E_d\) and \(E_c\) (or their ratio \(E_d/E_c\)), as well as the distribution of the repulsive forces between the inserted cations. The energies, \(E_d\) and \(E_c\), are affected, in turn, by the cation position, its size, cation–Mo interactions, and the anion nature, whereas the third parameter is related to the repulsion between the inserted cation, their sites’ arrangement, and their number for the group of sites, i.e., it depends on the intercalation level and the direction of the electrochemical reaction (insertion or extraction).

Important practical conclusion can be obtained from this work: In spite of the apparent ionic immobility for some compositions, the Mo\(_6\) clusters in CPs ensure a high diffusivity (at RT) of mono- and divalent cations with a wide spectrum of sizes. The reason for this unusual phenomenon is an efficient attainment of local electroneutrality by the Mo\(_6\) clusters upon cation insertion. Hence, a future development of new cathode materials for rechargeable Mg batteries should be focused on cluster-containing intercalation compounds.

**Acknowledgment.** Partial support for this work was obtained from the Israel-U.S. binational foundation (BSF). The Institut Laue Langevin is warmly acknowledged for providing the neutron facilities.

**Supporting Information Available:** Additional data relating to the mobility of different cations in CPs; maps of the cation sites for a variety of CPs, possible insertion mechanism for large cations, and typical examples of the diffusion analysis for the CPs with different cation mobility (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.