A review on the problems of the solid state ions diffusion in cathodes for rechargeable Mg batteries

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Abstract This work summarizes the results of our studies devoted to Mg ions mobility in Chevrel phases (CPs), $M_xMo_6T_8$ (M – metal, T = S, Se) and presents our vision of the problem of multivalent ions' diffusion in intercalation compounds. A simplified analysis of the main factors, which affect the activation energy barriers, as well as experimental data of Mg ions insertion into different hosts, show that low Mg ions mobility in common transition metal oxides or sulfides cannot be explained only by strong ionic interactions, but it is rather caused by a hard redistribution of the bivalent cations charge in inorganic materials. In contrast to these hosts, CPs allow for a high mobility of multivalent cations, because their unusual crystal structure with octahedral Mo_6-clusters enables a fast and efficient attainment of local electro-neutrality upon insertion of cations of high charge density. Analysis of diffusion pathways based on the detailed structural determinations sheds light on important aspects of the electrochemical behavior of CPs, such as partial Mg ions trapping in the course of reversible Mg insertion and the ways to avoid it.

Keywords Multivalent ions diffusion ·
Rechargeable Mg batteries · Chevrel phases

1 Introduction

The functioning of intercalation compounds and solid electrolytes has a common phenomenon, namely, solid-state diffusion of mobile ions. Elaboration of cathodes for rechargeable Mg batteries brought the diffusion problem of multivalent ions in inorganic hosts such as transition metal oxides and sulfides, to the forefront of solid state ionics. In fact, in spite of the evident similarity of the Li and Mg insertion into these hosts, almost all intercalation compounds, which prove themselves as suitable electrodes' materials in Li battery systems, show very poor electrochemical performance in Mg ions or complex solutions, due to a slow diffusion of Mg ions in the solids [1–10]. It is clear that the reason of the slow kinetics of Mg ions insertion into inorganic hosts is their divalent character; however the aspects of transport phenomena related to Mg ions insertion are not covered at all by the literature in electrochemistry, physical chemistry or solid state ionics. Some researchers speak in general about possible strong interactions between the inserted divalent cations with the anions and the cations of the hosts [10] or about high activation energies for site changes in cases where the inserted ions have high charge/radius ratio (e^2/r) [11].

A relatively fast and efficient Mg ions intercalation was observed for nano-crystalline materials [10], thin films [12] or nanotubes [13]. In such systems, the intercalation kinetics should be *a priori* much higher than that in the same materials with micrometric size particles. A few years ago we discovered [14–16] that Chevrel phases (CPs), Mo_6T_8 (T=S, Se), can insert reversibly and relatively fast, Mg ions even when comprising micrometric size particles, and hence, they can be used as practical cathodes materials for rechargeable Mg batteries. This discovery resulted from a lot of unsuccessful experiments of Mg ions insertion into well-known hosts for Li^+ ions insertion, as well as from the thorough literature analysis concerning the possibility of divalent ions intercalation into inorganic materials. Such analysis revealed that CPs are unique materials that allow

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for a relatively fast insertion of divalent cations including Zn^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Fe^{2+} [17–19].

In the previous studies, the interesting phenomenon of high divalent ions mobility in the CPs was ascribed to the existence of quasi-monovalent state of these cations as transients. These monovalent cations were assumed to be the result of a rapid one-electron transfer from the Mo_6T_8 matrix, e.g. $Zn^{2+}+e- \leftrightarrow Zn^+$ [17]. However, such explanation seems to be questionable, especially for Mg^{2+} ions. Thus, the main aim of our studies related to cathode materials for rechargeable Mg batteries, was to understand the reasons for the fast Mg transport in CPs and the poor electrochemical activity of other hosts with Mg ions.

In addition, our studies showed that the kinetics of the Mg ions diffusion in the CPs, is strongly affected by their composition and temperature. At ambient temperature, the selenide (Mo_6Se_8) shows excellent Mg ions mobility in the full intercalation range from 0 to two Mg^{2+} ions per formula unit [20], while a constant partial Mg ions trapping takes place in the sulfide CP ($Mg_xMo_6S_8$), i.e. part of the Mg^{2+} ions (about 20–25%) inserted initially into Mo_6S_8 electrodes in the course of their first cathodic polarization in appropriate Mg ions containing solutions, can be removed from the crystal structure of Mo_6S_8 electrochemically only at elevated temperatures [21]. Initially, this difference between the selenide and sulfide CPs was explained by the higher polarisability of the selenide framework [20], but the subsequent studies [22, 23] showed the crucial role of the CPs crystal structure' peculiarities in the trapping phenomenon.

This paper provides our vision of the problem of multivalent ions diffusion in intercalation compounds and summarizes results of our studies devoted to Mg ions mobility in CPs of different compositions.

2 Strong ionic interactions as a possible reason of slow Mg ions diffusion

The diffusion processes of ions in any solid host include two simultaneous steps: ions' hopping and redistribution of the ions' charge, in order to achieve local electro-neutrality [24]. However, whereas the hopping step may be independent on the type of materials, the second step is fundamentally different: In solid electrolytes, the electrostatic charge of the mobile ions is compensated by the opposite charge of the vacancies, while in intercalation compounds the insertion is associated with change in the oxidation state of the host cations (transition metals).

In order to analyze the effect of the cations' charge on the potential barrier upon hopping, let's compare the insertion of Li^+ and Mg^{2+} ions into the same host, for instance, into a classic cathode material, layered CoO_2.

Actually, the sizes of Li^+ and Mg^{2+} ions are almost the same (i.e. the cation–anion distances in the intercalation compounds, M_xCoO_2 (M=Li or Mg), are very close); thereby any variation in the activation energy of hopping is caused only by the difference in their charges. According to simple Coulomb interactions' considerations, it is clear that the chemical bonds between the Mg^{2+} cations and the anions of the host are twice stronger than those for Li^+ cations. However, the strength of these bonds related to the atom location in the lowest potential wells (in the MO_6 – octahedra for the layered M_xCoO_2) affects rather a potential energy of the intercalation compound, E_0, but not the potential barriers, E_a (Fig. 1).

The latter are affected by ionic interactions at the moment of the mobile ions being in the intermediate states or in the transport sites, in which the cation–anion distances are commonly effectively shorter then those in the wells. For instance, following the pathway of the hopping ions in the crystal structure of M_xCoO_2 from one octahedral site to another (Fig. 2a) [25–27], we can see two cation locations, which influence the potential barriers: 1 – the intermediate state upon cation squeezing between three oxygen atoms (coordination number CN=3), and 2 – tetrahedral transport site (CN=4). The lower is the CN, the shorter are the M–O distances.

In order to understand the factors that influence the value of the potential barrier, we have to analyze the forces that affect the intercalated ion in the latter sites. In the case that the intercalated cation is located in its normal (octahedral) sites, the attraction between all the ions is equal to the repulsion between them. If the distance between the ions decreases, the repulsion becomes higher than the attraction. As a result, the strong attractions between inserted divalent Mg^{2+} ions and the host anions should rather decrease the potential barriers by decreasing the repulsion upon squeezing, thus promoting the Mg ions diffusion. The effect is similar to that of a strong covalent bonding, which facilitates the diffusion [24]. Thus, it is impossible to explain the slow Mg diffusion in different hosts just by strong cation–anion interactions.

The next step has to be the analysis of the interactions between the inserted and host (permanent) cations. A normal minimal distance between the cations in the crystal

Fig. 1 Schematic presentation of activation energy E_a for ionic transport upon insertion processes
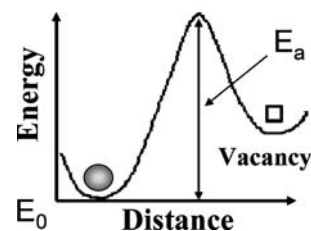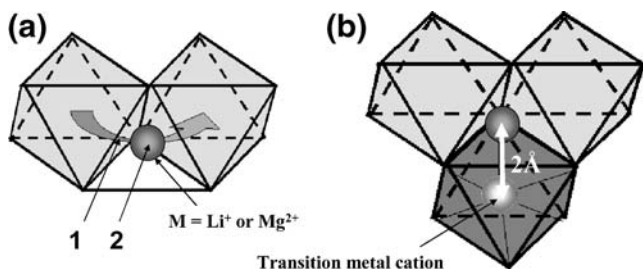
Fig. 2 The cation hopping in the crystal structure of M_xCoO_2: (a) the cation pathway from one octahedral site to another: *1* the intermediate state upon cation squeezing between three oxygen atoms (coordination number, CN = 3), *2* a tetrahedral transport site (CN = 4). (b) The cation–cation interactions: A short distance of 2 Å exists between the M (inserted) cation in the transport site and an adjacent Co atom

structure of transition metal oxides could not be shorter than 2.8 Å (The shorter distances testify about specific metal–metal interactions). For instance, in the layered $LiCoO_2$, the distance between all the adjacent cations is about 3 Å. However, at the moment when the intercalating Li^+ or Mg^{2+} ion is located in the transport tetrahedral site (Fig. 2b), the distance between this ion and the Co cation is about 2 Å instead of 2.8 Å. As a result, the repulsion between these cations is very strong, and twice higher in the case of Mg ions. Hence, the potential barrier in the layered CoO_2 host should be essentially higher for Mg^{2+} ions' transport than for the transport of Li^+ ions due to the stronger cation–cation repulsion.

Based on such simplified considerations, a fast Mg diffusion should be expected in the intercalation compounds, in which the ionic transport is not associated with strong cation repulsion, e.g. in the spinel-type materials. The crystal structure of the latter materials (e.g. $LiMn_2O_4$) is very similar to that of the layered $LiCoO_2$. It differs only by the transition metal distribution in the octahedral sites. As a result of this difference, the inserted ions can occupy not only the octahedral sites in the spinel framework, but also the tetrahedral sites. Thus, in the layered M_xCoO_2 the tetrahedral sites work only as transport sites with relatively high potential energy, while in spinel materials the tetrahedral sites are normal cation sites with relatively low potential energy [28]. This structural difference is associated with the lower repulsion between the transition metal and the intercalating cations for spinel-like hosts. In fact, we can divide the unit cell in the crystal structure of spinel materials to 8 segments (Fig. 3). The cations of the transition metal are located in 4 of them, while the transport of the intercalating cations, takes place in another 4 segments. Thus, we can expect that the potential barrier in spinel structures, should be lower than in layered compounds, and hence, the insertion kinetics should be faster in the former systems. Actually, a relatively fast ionic transport of polyvalent ions in β'' alumina with spinel-like

crystal structure [24] confirms this expectation. Consequently, one would recommend, *a priori*, materials with spinel crystal structure, as possible hosts for Mg ions intercalation.

However, the attempts made in the framework of this study to insert essential amount of Mg ions into classical spinel materials such as MnO_2 and cubic (c−)TiS_2 with spinel type structure, were unsuccessful. Relatively high electrochemical activity of (c−)TiS_2 with Mg ions (in Mg ions containing non-aqueous solutions) was found only for a first cycle at elevated temperatures (Fig. 4) [29]. Similar data were obtained by other researchers [3], who performed chemical intercalation of Mg in these materials: A maximal intercalation level reached for Mg_xTiS_2 was x=0.22 for the layered compound and x=0.25 for the spinel one. According to these results, it can be suggested that another factor, besides strong repulsion among cations, is responsible for the slow Mg ions diffusion in common inorganic hosts.

3 Hard redistribution of the ions charge as the main problem of the multivalent ions' diffusion in inorganic hosts

As was mentioned in the previous section, ions insertion into intercalation compounds is associated with changes in the oxidation state of the host cations (of transition metals). Thus, in order to compensate two charge units associated with insertion of one Mg^{2+} ion, the adjacent transition metal ion must change its oxidation state by two electrons (Pauling's rule of local electro-neutrality). It is clear that this process should be difficult for most of commonly
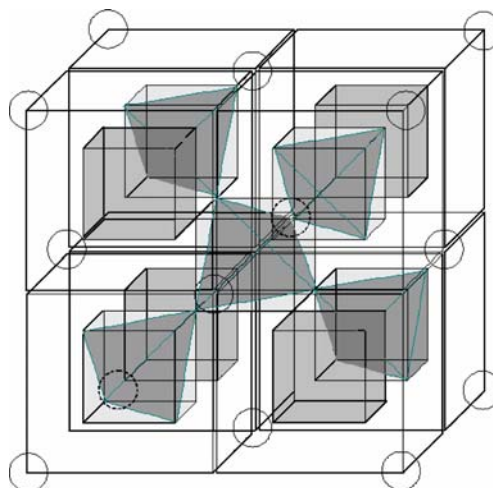

Fig. 3 Separate cation distribution in the spinel crystal structure: The transition metal cations form tetrahedra located in 4 of the 8 segments of a unit cell. Li^+ cations can occupy either tetrahedral sites (part of these sites is marked by *circles* and another part is located in the centers of 4 *dark-grey cubes*), or the octahedral sites in 4 of the 8 vertexes of the same *dark-grey cubes*
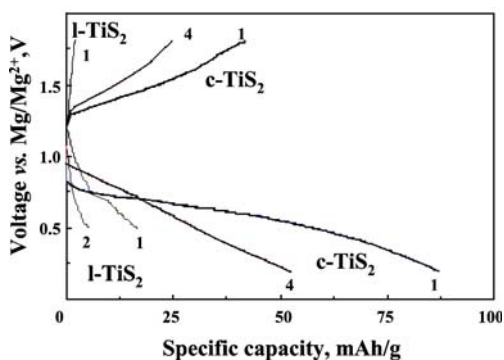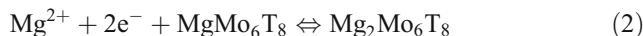
Fig. 4 Comparison of the chrono-potentiometric behavior of composite electrodes comprising the active masses: c-TiS$_2$ (spinel like) and l-TiS$_2$ (layered material), in THF solutions of the complex salt Mg(AlCl$_2$-BuEt)$_2$ 0.25 M, at 60°C, constant current: 0.1 mA/cm^2. The first Mg ions insertion–deinsertion cycle and the subsequent second Mg ions insertion processes are seen with the l-TiS$_2$ electrode, while the 1st and 4th Mg ions insertion–de-insertion cycles are presented for the c-TiS$_2$ electrodes (and demonstrate a pronounced decay in the capacity) [19]

studied intercalation compounds: First of all, not all the transition metals can undergo electrochemical processes with a charge transfer of more than one electron per ion. In addition, the abrupt change in the oxidation state of transition metal cations upon multi-electron red-ox processes should result in the drastic local deformations in the crystal structure of the host, which can be in many cases, thermodynamically unfavorable. For instance, the size of the Mn ion increases by a factor of 1.75 due to the change of its formal charge from +4 to +2. Hence, it seems natural that common intercalation compounds show poor activity in processes of Mg ions insertion.

In contrast to most of the ionic (inorganic) hosts, commonly studied in connection with electrochemical intercalation reactions, the crystal structure of CPs [30, 31] is composed of the Mo$_6$T$_8$ blocks, e.g. octahedral clusters of six Mo atoms with metal–metal chemical bonds, which are surrounded by eight chalcogen ions. Such a Mo$_6$-octahedron can be regarded as a single transition metal ion that can accommodate up to 4 electrons (compare to one or two electrons for a usual transition metal ion). Upon insertion of one Mg^{2+} ion per formula unit, the formal charge of the individual Mo ion in the cluster changes only by 1/3 electron. In addition, this insertion is associated with minimal dimensional variations in the crystal structure. In fact, upon insertion of two Mg ions per formula, the distance between Mo atoms in the cluster decreases by no more than 6%, while the distance between the Mo clusters increases by about 9%. Thus, the unusual activity of CPs in the reversible processes of Mg ions insertion/extraction can be attributed to the presence of Mo clusters in the crystal structure of these materials.

4 The origin of partial Mg trapping in CPs and the ways to avoid it

Our studies [20, 21] showed that Mg insertion into Mo$_6$S$_8$ and Mo$_6$Se$_8$ proceeds *via* two stages:

$$Mg^{2+} + 2e^- + Mo_6T_8 \Leftrightarrow MgMo_6T_8 \qquad (1)$$

$$Mg^{2+} + 2e^- + MgMo_6T_8 \Leftrightarrow Mg_2Mo_6T_8 \qquad (2)$$

Hence, cyclic voltammograms (CV) measured at slow enough potential scan rates (i.e. at rates that reflect the thermodynamic behavior of these systems, beyond diffusion control) with electrodes comprising these Mo$_6$T$_8$ compounds as the active mass in the appropriate Mg salt solutions, should present two peaks of similar intensity for the Mg ions insertion processes and two conjugate peaks for their extraction. Figure 5 compares typical steady-state slow-scan rate cyclic voltammograms (SSCV) of Mg ions intercalation processes into Mg$_x$Mo$_6$S$_8$ and Mg$_x$Mo$_6$Se$_8$ (x<0<2) electrodes (the fifth cycle). As can be seen, for the selenide CP host, the electrochemical results are in a complete accordance with the reactions (1) and (2) above. In contrast, for the sulfide, the peak associated with the first stage of Mg ions insertion is essentially smaller than that of the second stage. Upon Mg ions extraction, the CV peak related to the second stage of the Mg ions de-intercalation (from MgMo$_6$S$_8$) is shifted to essentially high potential, it is very broad and reflects less charge transfer than expected for a full de-magnesiation process.

By a combination of chrono-potentiometric experiments at different temperatures and phase analyses (X-ray diffraction) of the electrode materials at different intercalation stages, it was found [21] that the full theoretical capacity corresponding to the insertion of two Mg^{2+} cations per
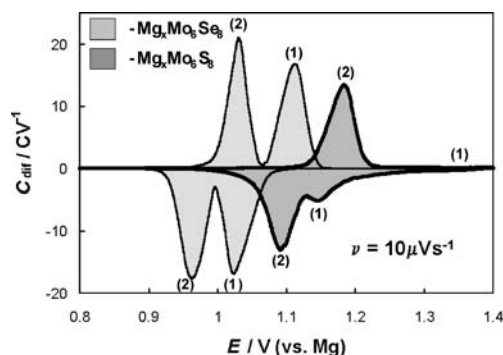

Fig. 5 Typical slow scan rate, steady state CV measured with electrodes comprising Mo$_6$S$_8$ and Mo$_6$Se$_8$, upon reversible intercalation with Mg ions in THF solutions of the complex salt Mg (AlCl$_2$BuEt)$_2$ 0.25 M at 25^{0}C. The *numbers in the parentheses* correspond to the reactions (1) and (2)

formula (122 mAh/g), can be obtained upon the first cathodic polarization (i.e. magnesiation) of Mo_6S_8 electrodes. However, the process of the Mg ions extraction from the sulfide can be completed only at elevated temperatures because of some constant Mg ions' trapping at R.T. in this host. Since Mo_6S_8 is considered as a main cathode material for rechargeable Mg batteries, and a full utilization of this material in Mg battery systems is critical for practical aspects, it was highly important to clarify the reasons for the trapping effect in the sulfide and its absence in the selenide host.

In order to understand the charge trapping mechanism, the analysis of the diffusion pathway of Mg^{2+} cations in the CPs hosts was performed. This analysis required knowledge of the detailed crystal structure of the intercalation compounds, which should include not only the atomic arrangement in the hosts, but also the distribution of the inserted cations. By combined X-ray and neutron diffraction it was shown [23] that the crystal structure of $Mg_xMo_6S_8$ (x=1 and 2) is similar to that of classic CPs with a rhombohedral symmetry. The sites available for cation insertion form an infinite three-dimensional framework (See the insert in the right corner of Fig. 6a), but according to their location between the Mo_6T_8 cubes they can be separated into individual groups. Each group includes 12 sites (Fig. 6a): inner and outer rings, which differ by their potential energy: The outer sites are less favorable, because they are closer to the Mo atoms. As a result, in the rhombohedral sulfide, $MgMo_6S_8$, one Mg^{2+} cation per formula unit is statistically distributed between 6 inner sites. In $Mg_2Mo_6S_8$, additional cation occupies one of the 6 outer sites (The inner sites for the second cations are not available because of the strong repulsion between two Mg^{2+} ions).

Note that the diffusion of Mg ions in the CPs bulk, should involve a cation motion between different groups of sites. Thus, in order to ensure this diffusion, the cation has to pass from initial inner site to the adjacent outer site of the same group, after that it moves to a new outer site of another group and so on. However, in $MgMo_6S_8$, the six inner sites, available for Mg ions insertion, are too close to each other. As a result, instead of moving from one group of sites to another one, part of the inserted cations prefer to move in the same group of the inner sites (a circular motion instead of progressive transport in the material bulk).

Interestingly, examining a diffusion rate for a separate, elementary jumping of single inserted cations, there are no slow diffusion processes in CPs. The cation circuit transport may be very fast, but the factor that limits the kinetics of the overall diffusion in the bulk, is the hopping between inner and outer sites. Thus, the fast, local, Mg circuit motion is accompanied by slow diffusion in the electrode bulk. Only the insertion of the second cation in the same
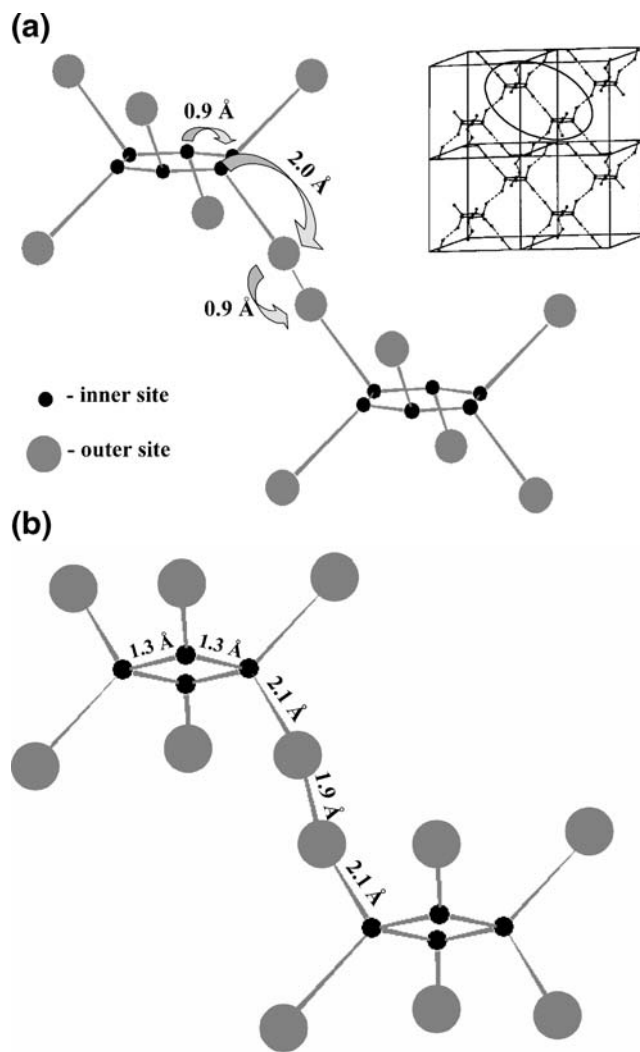

Fig. 6 Arrangement of cation sites in $MgMo_6T_8$: (a) Two adjacent groups of cation sites (12+12) in the crystal structure of the sulfide, $MgMo_6S_8$, marked by ellipse in the *insert*. The *insert* presents the three-dimensional framework of cation sites [35]. (b) Two adjacent groups of cation sites in the crystal structure of the selenide, $MgMo_6Se_8$

group of sites allows for the progressive Mg^{2+} ions transport. This additional inserted ion is located initially in one of the outer sites of the same group, but finally moves to the adjacent group and occupies a vacant inner site with minimal potential energy. It means that the phase boundary "$MgMo_6S_8 \leftrightarrow Mo_6S_8$" moves only in the presence of two Mg^{2+} ions in the groups of sites close to the boundary. As a result, the insertion process at the first stage occurs at lower voltage than the characteristic potential of the reaction (1) and with relatively slow kinetics. In contrast, the second stage of the Mg ions insertion is characterized by a fast kinetics and very low over-voltage.

The repulsion between two Mg^{2+} ions (per formula unit) exists also upon extraction of the first Mg^{2+} ion from

$Mg_2Mo_6S_8$. As a result, there is no kinetic problem at all in this stage of the electrochemical process. However, at the second extraction stage, when all the cathode material has only one Mg atom per formula unit, there are no additional Mg^{2+} ions, which can promote the progressive diffusion of Mg ions by $Mg^{2+} - Mg^{2+}$ repulsion. As a result, part of the Mg^{2+} ions move in a circular manner between the inner sites, and in fact are trapped in the sulfide CP host. In order to overcome the activation energy barriers existing between the inner and outer sites and to complete the electrochemical Mg ions extraction from the sulfide CP, it is necessary to increase the energy of the thermal vibrations in the material by elevating its temperature. Indeed, the trapping effect completely disappears at 60°C.

In contrast to the sulfide CP electrodes, the electrochemical Mg ions insertion into the selenide host, Mo_6Se_8, leads to a triclinic distortion and to the changes in the cation sites' geometry (Fig. 6b) [22]. Instead of the 6 equivalent inner sites existing in the sulfide host, in the selenide, there are two pairs of sites with relatively close potential energy. The distances between these sites in the selenide are larger than that in the sulfide. This leads to effectively smaller difference between the hopping lengths for inner–inner and inner–outer sites in $MgMo_6Se_8$ as compared to $MgMo_6S_8$. This peculiarity of the selenide crystal structure, together with the higher polarizability of its anionic framework, result in the absence of Mg ions trapping phenomenon at all, as well as in high Mg ions mobility along the entire intercalation process, even at R.T.

Once the trapping mechanism is understood, it was possible to develop two approaches to alleviate this negative phenomenon: 1) to change the geometry of the cation arrangement by a partial substitution of sulfur by selenium in the CP hosts [32] and 2) to avoid the stage of the full cation extraction by using Mg insertion into ternary CPs, such as $Cu_yMo_6S_8$ ($0<y<1$), which behave fully reversibly in ethereal complex Mg salt solutions [33]. In the former case, replacement of 2 sulfur atoms per formula unit by selenium, does not affect too strongly the theoretical capacity of the host, but enable to utilize mot of the active material at R.T., even at high rates of electrochemical processes [32]. In the latter case, insertion of Mg ions into $CuMo_6S_8$ is accompanied by reduction and extrusion of Cu. In the reverse (anodic) process, the extruded Cu metal is oxidized, and hence, Cu cations are inserted back to the CP structure, while pushing the Mg^{2+} ions from the inner to the outer sites. As a result, the Mg^{2+} cations can move freely throughout the host bulk, up to their full removal from the cathode material. Consequently, a very fast and fully reversible Mg ions insertion is possible with $CuMo_6S_8$ electrodes, even at R.T. [34].

5 Conclusion

This work presents a simplified analysis of the main factors, which affect the kinetics of electrochemical cations insertion into various inorganic hosts. This analyses, as well as experimental data on Mg ions insertion processes into different intercalation compounds, show that low Mg ions mobility in well studied inorganic hosts (which can serve as very good Li intercalation electrodes' materials) cannot be explained only by strong ionic interactions (e.g. cation–anion attraction or cation–cation repulsion), but it is rather caused by a hard redistribution of the charge of the inserted multivalent cations in these materials. In contrast to many common hosts (transition metal oxides and sulfides), CPs allow for intercalation of multivalent cations into them, at high mobility, because their unusual crystal structure with octahedral Mo_6-clusters enables a fast attainment of local electro-neutrality, which is necessary for such an insertion. As a result, CPs can be suggested as unique cathode materials for rechargeable Mg batteries.

Interesting peculiarities in the electrochemical behavior of the CPs in the course of Mg ions insertion reactions could be understood based on the rigorous structural analyses of the intercalation products. For instance, we were able to outline the most favorable routes for Mg ions diffusion in the crystal structure of $Mg_xMo_6T_8$ (T = S, Se, $x=1$ and 2). It was shown that partial Mg ions trapping, which is observed at R.T in the sulfide CP host, results from a unique ring arrangement of closely set (inserted) cations sites with a relatively low potential energy. This arrangement leads to a circular motion of part of the inserted Mg cations in the course of de-intercalation, instead of a progressive diffusion in the material bulk. This phenomenon is relevant only upon extraction of the last Mg cation per formula unit, because the repulsion between the Mg^{2+} cations in $Mg_2Mo_6S_8$ facilitates the Mg ions transport in the material bulk. Mg ions trapping does not occur at all with the selenide CP host, which insert Mg ions very fast, at full capacity, even at R.T. Thus, high Mg ions mobility is exhibited in this host throughout the entire intercalation process. This difference in the electrochemical behavior of the sulfide and selenide host is related not only to higher polarizability of the selenium framework, but mostly to the different cation sites' geometry in $MgMo_6S_8$ and $MgMo_6Se_8$.

Two ways to prevent Mg trapping in CPs were proposed: 1) to change the geometry of the cation arrangement by a partial sulfur substitution by selenium (e.g. using $Mo_6S_6Se_2$) and 2) to avoid the stage of the full extraction of the inserted cations by using ternary CPs, such as $Cu_yMo_6S_8$. In the latter case, Cu is extruded upon Mg ions

insertion and is oxidized to Cu ions, which are re-inserted while pushing out the Mg ions, in the course of de-intercalation (the anodic, charging process). As a result, the Mg^{2+} cations can move freely throughout the material bulk up to their full removal from the cathode material. It was shown that the above hosts behave fully reversibly in ethereal complex Mg salt solutions. Both these ways enable utilize the full capacity of these hosts at high rates and low temperature, on the expense of giving up too much in the theoretical capacity.

References

1. J.P. Pereira-Ramos, R. Messina, J. Perichon, J. Electroanal. Chem. **218**, 241 (1987)
2. T. Gregory, R. Hoffman, R. Winterton, J. Electrochem. Soc. **137**, 775 (1990)
3. P.G. Bruce, F. Krok, J. Nowinski, V.C. Gibson, K. Tavakkoli, J. Mater. Chem. **1**, 705 (1991)
4. P. Novak, J. Desilvetro, J. Electrochem. Soc. **140**, 140 (1993)
5. F. Joho, P. Novak, O. Haas, R. Nesper, Chimia **47**, 288 (1993)
6. P. Novak, W. Scheifele, O. Haas, J. Power Sources **54**, 479 (1995)
7. M.E. Spahr, P. Novak, O. Haas, R. Nesper, J. Power Sources **54**, 346 (1995)
8. P. Novak, R. Imhof, O. Haas, Electrochim Acta **45**, 351 (1999)
9. K. Makino, Y. Katayama, T. Miura, T. Kishi, J. Power Sources **99**, 66 (2001)
10. G.G. Amatucci, F. Badway, A. Singhal, B. Beaudoin, G. Skandan, T. Bowmer, I. Plitz, N. Pereira, T. Chapman, R. Jaworski, J. Electrochem. Soc. **148**, A940 (2001)
11. C. Ritter, C. Noldeke, W. Press, U. Stege, R. Schollhorn, Zeitschrift Fur Phisik B **92**, 437 (1993)
12. T.S. Sian, G.B. Reddy, Solid State Ionics **167**, 399 (2004)
13. Z.-L. Tao, L.-N. Xu, X.-L. Gou, J. Chen, H.-T. Yuan, Chem. Comm. **18**, 2080 (2004)
14. D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moskovich, E. Levi, Nature **407**, 724 (2000)
15. D. Aurbach, Y. Gofer, Z. Lu, A. Schechter, O. Chusid, H. Gizbar, Y. Cohen, V. Ashkenazi, M. Moskovich, R. Turgeman, E. Levi, J. Power Sources **97**, 28 (2001)
16. D. Aurbach, I. Weissman, Y. Gofer, E. Levi, Chem. Record **3**, 61 (2003)
17. E. Gocke, W. Schramm, P. Dolscheid, R. Schollhorn, J. Solid State Chem. **70**, 71 (1987)
18. R. Schollhorn, M. Kumpers, J.O. Besenhard, Mat. Res. Bull. **12**, 781 (1977)
19. C. Fischer, E. Gocke, U. Stege, R. Schollhorn, J. Solid State Chem. **102**, 54 (1993)
20. M.D. Levi, E. Lancry, E. Levi, H. Gizbar, Y. Gofer, D. Aurbach, Solid-State Ionics **176**, 1695 (2005)
21. E. Lancry, E. Levi, Y. Gofer, M. Levi, G. Salitra, D. Aurbach, Chem. Mater. **16**, 2832 (2004)
22. E. Levi, E. Lancry, A. Mitelman, D. Aurbach, O. Isnard, D. Djurado, Chem. Mater. **18**, 3705 (2006)
23. E. Levi, E. Lancry, A. Mitelman, D. Aurbach, G. Ceder, D. Morgan, O. Isnard, Chem. Mater. **18**, 5492 (2006)
24. A.R. West, Basic Solid State Chemistry (John Wiley & Sons, Chichester-New York 1988), p. 313
25. A. Van der Ven, G. Ceder, Electrochem. Solid-State Lett. **3**, 301 (2000)
26. A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesh, Phys. Rev. B **6418**, 4307 (2001)
27. A. Van der Ven, G. Ceder, J. Power Sources **97–98**, 529 (2001)
28. M.M. Thackeray, J. Prog. Batteries Battery Mater. **14**, 54 (1995)
29. N. Amir, Y. Vestfried, O. Chusid, Y. Gofer, D. Aurbach, J. Power Sources **174**, 1234 (2007)
30. Ø. Fisher, M. B. Maple, Topics in Current Physics: Superconductivity in Ternary Compounds I (Springer, Berlin 1982)
31. K. Yvon, in Current Topics in Material Science: Vol. 3, ed. By E. Kaldis (Elsevier, Amsterdam 1979)
32. D. Aurbach, G.S. Suresh, E. Levi, A. Mitelman, O. Mizrahi, O. Chusid, M. Brunelli, Adv. Mat. **19**, 4260 (2007)
33. E. Levi, A. Mitelman, D. Aurbach, M. Brunelli, Chem. Mater. **19**, 5131 (2007)
34. E. Levi, A. Mitelman, E. Lancry, M.D. Levi, M. Brunelli, D. Aurbach, Chem. Comm. 4212 (2007)
35. T. Uchida, Y. Tanjo, M. Wakihara, M. Taniquchi, J. Electrochem. Soc., **137**, 7 (1990)