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On the Way to Rechargeable Mg Batteries: The Challenge of New Cathode Materials[†]

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To initiate wider discussion about promising research directions, this paper highlights a number of challenges in the development of rechargeable Mg batteries, especially those related to the slow solid-state Mg diffusion in common hosts. With a focus on the intercalation mechanism, we compare for the first time different strategies proposed in the literature for developing Mg battery cathodes, like the use of (i) nanoscale cathode materials; (ii) hybrid intercalation compounds containing bound water or other additional anion groups that can presumably screen the charge of the inserted cations, (iii) cluster-containing compounds with efficient attainment of local electroneutrality. This comparative analysis shows that cathodes whose function is based on a combination of the two first strategies, e.g., V_2O_5 gels and their hybrids, can exhibit relatively high voltage and capacity upon Mg insertion, but their kinetics is insufficiently fast. A proper intercalation mechanism for such materials is still unknown, but their relatively slow cation transport seems to be intrinsic: The paradox is that the high capacity testifies Mg insertion into crystal sites with incomplete charge screening. In contrast, the high rate capability and exclusively stable cycling of cathodes based on Chevrel phases (Mo_6-cluster- containing compounds) are appropriate for Mg battery design, but they offer low energy density because of the low voltage. On the basis of the knowledge of the intercalation mechanism in these phases, we believe that the future search for cathode materials in rechargeable Mg batteries should be focused on new cluster-containing intercalation compounds with higher capacity and working potential.

Introduction

The initiative to develop secondary Mg batteries was to present a competitive alternative to Li systems, comparable in electrochemical parameters, but safer and less expensive.[1] Of the few potential anode materials, magnesium seems to be the most promising candidate, because of its "green" character, high natural abundance in the Earth's crust (13.9% as compared to 7×10^{-4} % for Li), and atmospheric stability. Thus, in the end of 1980th, several research groups directed their efforts toward the elaboration of Mg batteries, based on the same principles as in lithium cells: electrochemical magnesium deposition\dissolution for the anode reaction, and cation insertion for the cathode. However, whereas the last 20 years proved to be very successful for Li batteries, the development of Mg systems did not make it to the production line. It appears that contrary to lithium, magnesium electrochemistry suffers from several serious limitations, such as

1. Anode/electrolyte incompatibility. Magnesium, like lithium, develops surface films upon exposure to oxygen, humidity, and most polar organic solvents, as a result of reduction reactions. However, in contrast to lithium, the interphase thus formed, is a real passivation barrier, since it is both electron and ion insulating.[1,2] Thus, in most polar organic electrolytes, such as those common in lithium batteries, magnesium anodes do not function as reversible electrodes, rendering a fully passivated, useless electrode.

Nevertheless, screening the scientific literature reveals that most of the studies devoted to Mg cathodes were performed in such electrolytes (Some of the works did not use Mg anodes, but rather different sources of Mg^{2+} ions), frequently, without proper discussion regarding the limitations of the anode electrochemistry. Hence, once any of these cathode materials proves viable for practical use, a full compatibility study of these materials with proper electrolyte should be necessary. Such a study will be particularly crucial for hydrated cathodes because of incompatibility between water and magnesium or between water and some of the feasible electrolytic solutions.

2. Narrow electrochemical windows of the electrolyte solutions. Organohaloaluminate/ether electrolytes, which do enable reversible Mg dissolution, exhibits relatively narrow electrochemical stability window, of up to 2.2 V vs. Mg (~2.8 V vs. Li/Li^+).[3] Thus, the use of these electrolytes limits greatly the choice of cathodes for Mg

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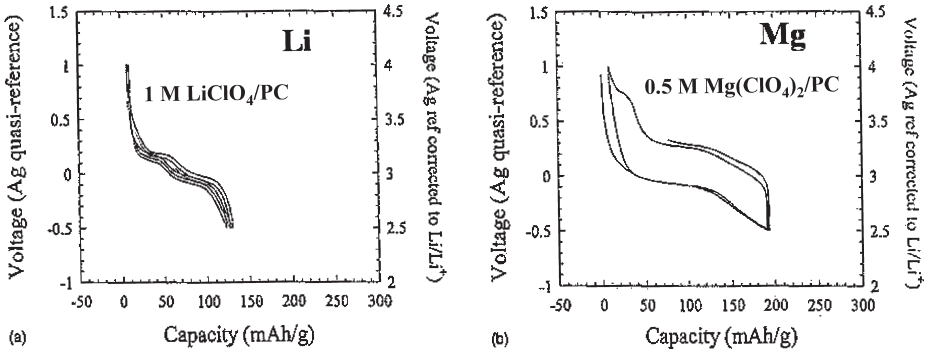

Figure 1. Chronopotential curves of (a) Li and (b) Mg insertion into nanocrystalline V_2O_5. Constant current is equal to 7.6 mA h/g, according to ref 5. Reprinted with permission from ref 5. Copyright 2001 Electrochemical Society.

battery and ultimately, its potential specific energy. In addition, these electrolyte systems are based on organometallic compounds of aluminum and magnesium, materials that are known to be hazardous. Dealing with ways to widen the electrochemical windows of electrolyte solutions for Mg batteries is beyond the scope of this paper.

3. Slow solid-state diffusion of Mg^{2+} cations. Until now, only one material family, namely, Chevrel phases, $M_xMo_6T_8$ (M = metal, T = S, Se) in their usual microcrystalline state, allows for fast and reversible Mg insertion at ambient temperatures.[4] The majority of the intercalation compounds, proved to be good Li cathodes, show poor, if any, electrochemical activity with Mg, usually because of the exceedingly slow solid-state diffusion of the divalent cations. With those materials that do show at least some electroactivity with magnesium, the slow kinetics is evident from (i) a low intercalation level (low practical capacity) that can be reached with Mg insertion and (ii) a very large difference between the discharge and charge potentials obtained during the electrochemical processes (The higher this difference, the further away is the electrode from the equilibrium potential, and the higher is the kinetic limitation). For instance, Figure 1 demonstrates[5] that Li insertion and deinsertion into/from nanocrystalline V_2O_5 occur at close potentials, while in the case of Mg system under similar experimental conditions, these potentials diverge by ca. 400 mV. In spite of the obvious problem of slow diffusion, the reviews[1,6] devoted to Mg cathodes are rather focused on the specific results obtained for various hosts, but not on the mechanism of ionic transport. The slow Mg diffusion was generally assigned to strong Mg interactions with the anions and the cations of the hosts[5] or to the polarization effect of Mg^{2+} cations with a high charge/radius ratio.[7]

4. Relatively low specific energy of Mg battery. For the identical hosts, the theoretic specific energy of Mg batteries is fundamentally lower than that of Li batteries. In general, this energy can be presented as a product of the theoretical cathode capacity (that should be independent of the guest ions) and the average voltage V. For the latter

$$V_M(x) = -(\mu_M^{cathode} - \mu_M^{anode})/F \quad (1)$$

where F is the Faraday constant and $\mu_M{}^{cathode}$ and $\mu_M{}^{anode}$ are the chemical potentials of M (M = Li or Mg) in the cathode and the anode, respectively. Thus, the difference ΔV between voltages of Li and Mg batteries with the same host is

$$\Delta V(x) = [(\mu_{Mg}^{anode}) - \mu_{Li}^{anode}/F] + [(\mu_{Li}^{cathode} - \mu_{Mg}^{cathode})/F] \quad (2)$$

Taking the reversible potential of Li and Mg electrodes from the electrochemical series (−3.05 and −2.38 V vs normal hydrogen electrode, respectively[8]), the first member in eq 2 is 0.67 V. The exact value of the second member is difficult to predict, but it is clear that it should be positive: As a rule of thumb, the chemical potentials of Mg in the same hosts are more negative than that of Li because of the lower potential energy of compounds with divalent cations.

According to the Kapustinskii equation,[9] the potential energy U of an ionic compound is proportional to the product of the ion number n in the formula unit and the ionic charges q_i divided by the sum of the ionic radii (note that the Li^+ and Mg^{2+} radii in solids are very similar). For instance, for the products of the cation insertion into titanium disulfide, $LiTiS_2$ and $Mg_{0.5}TiS_2$, the difference in the potential energies is related mainly to the different numbers n ($n_{Li} = 4$ and $n_{Mg} = 3.5$ for Li and Mg compounds, respectively) and charges of the inserted cations ($q_{Li} = 1$ and $n_{Mg} = 2$). Thus, the ratio $U_{Mg}/U_{Li} \approx 3.5 \times 2/4 \times 1 = 1.75$.

Finally, the voltage expected with a Mg battery is about 1 V lower than that of the Li battery with the same cathode material. In fact, replacing Li−TiS_2 with Mg−TiS_2 results in a decrease in the average discharge voltage of the battery from 2.1 to 1.1 V.[10] A similar change takes

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place for the Chevrel phase, Mo_3T_4 (T = S, Se).[4] As a result of the low operating voltage and the low specific energies which were measured with a part of the known hosts, the interest in Mg batteries decreased. Currently, magnesium batteries are suggested as a possible alternative to low specific energy systems, such as lead-acid and Ni−Cd systems.[8]

Interestingly, in a recent review by P. Novak,[1] it was stated that Mg insertion in most cases occurs at the same potential region as that of Li insertion (The potentials were recalculated against Li/Li^+). Moreover, according to refs,[11,12] the potentials of Mg intercalation into V_2O_5 (gel) were found to be higher than those of Li. Unfortunately, the authors did not comment on this interesting, and potentially key, phenomenon.

As can be concluded from these selected examples, the complexities in the electrochemical behavior of Mg batteries were not fully pointed out in the available scientific studies. We believe that a profound understanding of the critical bottlenecks on the way to Mg batteries is crucial for progress in the right direction. Recently,[13,14] we presented a new concept regarding the mechanism of multivalent ion diffusion in intercalation compounds. It was shown that the poor Mg mobility in common transition metal oxides or sulfides could not be explained only on the grounds of strong ionic interactions. We have shown that it is rather dominated by the complexity in the redistribution of the bivalent cation charge within the local crystal structure of the inorganic materials. The aim of this article is to highlight the origin of the problems mentioned above and to analyze the different strategies proposed for their solutions, especially those related to Mg cathodes.

Different Strategies to Improve Mg Insertion Kinetics

Drastic Decrease in the Particle Size for the Active Material. A common way to improve electrode kinetics is to decrease the particle size of the active materials, either by milling or direct synthesis in nanometric scale. Such a decrease results in shorter diffusion lengths, i.e., it ensures more efficient and rapid access of the inserted cations from the electrolyte solution to the available sites in every part of the host volume. Moreover, in the event that the surface area is significantly large, it may work in a similar way as in the electroadsorption-based supercapacitors. This scheme was tested in most of the works devoted to Mg cathodes. For instance, it was shown[15,16] that a maximal intercalation level of x, which can be reached for microsize Mg_xTiS_2 by chemical or electrochemical reaction at room and elevated (60 °C) temperatures, is equal to 0.22 and 0.37, respectively (the theoretical value is equal to 0.5), whereas the capacity decreases severely upon the first four cycles. Better results ($x = 0.49$ for $C/47$ and 0.29 for $C/7$, less degradation upon cycling) were demonstrated for TiS_2 nanotubes at RT, but in contrast to the microcrystalline materials, cycling at elevated temperature was associated with considerable capacity fading.[10] It is quite possible that the high surface area of the cathode material enhance the chance for undesirable, harmful reactions with the electrolyte solution, 1 M $Mg(ClO_4)_2$/acetonitrile. A problematic Mg deposition[17] in the latter solution may also be a possible reason for the deterioration in the cell performance with cycling.

Shielding of the Mg^{2+} Ion Charge. It is clear that the slow transport of Mg^{2+} ions in common hosts is related to their divalent character. Thus, it is logical to suggest that the insertion kinetics might be greatly improved when additional anion groups around the inserted cations cointercalate and shield the charge of Mg^{2+} ions within the intercalation compound. In fact, it was shown[18] that poor Mg insertion into microcrystalline V_2O_5 can be essentially improved by the addition of water to the electrolyte solution (e.g., 1 M $Mg(ClO_4)_2$ + 1 M H_2O/acetonitrile). The authors related this effect to the preferential solvation of the Mg^{2+} ions by water in the electrolyte and the reversible cointercalation of the H_2O molecules between the atomic layers of the host, where the solvation shell partially shields the charge of the Mg^{2+} cations (Figure 2). In spite of the improvement, the electrochemical behavior of the system was far from being practical: The highest capacity reached in the first cycle by slow cycling voltammetry (0.02 mV/s, ~7 mg of the active material) was less than one-third of the theoretical one (170 vs 589 mA h/g of V_2O_5), and it drastically decreased upon subsequent cycling (down to 50 mA h/g after five cycles). In addition, such a system would also have serious disadvantages, as follows.

(1) Insertion/deinsertion of big guest ionic groups (e.g., six H_2O molecules around each Mg^{2+} cation, or two water layers coinserted between V_2O_5 sheets[19,20]) may be destructive because of the high local deformations in the crystal structure of the hosts.

(2) It was shown[21,22] that the maximum intercalation levels attainable with alkali ions in solvated phases is fundamentally lower (typically in the range of 0.1−0.5) than that of nonsolvated ions, e.g., $x = 1$ for Li_xTiS_2 and $x = 0.5$ for $Li_x(H_2O)_yTiS_2$.

(3) The use of the wet electrolytes should be problematic because of the water reaction with metallic Mg anode.

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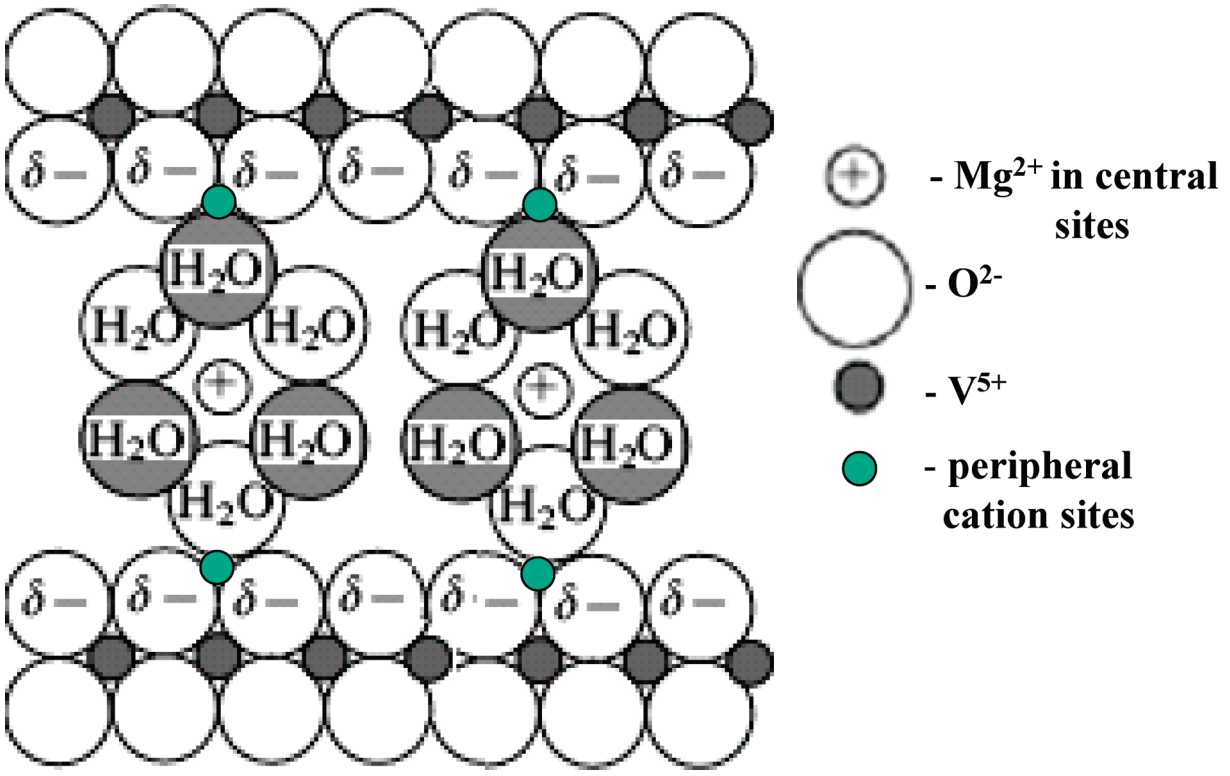

Figure 2. Crystal structure model of hypothetic intercalation compound with solvated Mg^{2+} ions located between the V_2O_5 layers.

To avoid the latter effect, in the subsequent works the researchers used hosts already containing water in their crystal structure, e.g., hydrated vanadium bronze, $Mg_x(V_30_8)_2 \cdot 3H_2O$, obtained on the basis of V_2O_5 gel.[23] It was expected that the H_2O molecules, located between nanometric layers of the host, would remain constantly bound in the crystal structure (i.e., they would not leach out upon cation deintercalation), thus preventing undesirable water reaction with the anode. Actually, for the first cycle, the electrochemical characteristics of the bronze in dry acetonitrile were similar to those of the microcrystalline V_2O_5 in the wet electrolyte (see above). However, in contrast to expectations, continuous cycling resulted in water ejection from the crystal structure of the host, as well as in rapid capacity fading.[23]

Significantly better results were presented for dry V_2O_5 gels:[11,12,24] an almost theoretical capacity (589 mAh/g of V_2O_5 or two Mg^{2+} ions per formula unit, i.e., V^{5+}/V^{4+} reduction) obtained by chemical[12] and slow electrochemical[11] Mg intercalation with rather stable cycling (Figure 3a).[11] Moreover, the $Mg-V_2O_5$(gels) systems showed an unusually high operating voltage (Figures 3b, c). However, the power density of the cells was only about one-tenth of similar Li systems because of the relatively slow kinetics of Mg insertion.[11] Thus, the key question is whether it possible to improve Mg^{2+} ion transport within these compounds, or is the slow solid-state diffusion their unavoidable intrinsic property?

Note that the electrochemical characteristics mentioned above were obtained for completely different cell designs: Carbon particles covered by thin layer of V_2O_5 xerogel were tested vs Mg anode in 1 M $Mg(ClO_4)_2$/acetonitrile;[11] V_2O_5 aerogels formed by supercritical drying with liquid CO_2 were examined vs product of chemical intercalation, $Mg_{0.6}V_2O_5$, in 0.1 M $Mg(CF_3SO_3)_2$/propylene carbonate[12] or vs carbon paper in 0.1 M $Mg(ClO_4)_2$/propylene carbonate.[24] In addition, the materials were studied by different electrochemical methods; thereby it is difficult to compare the results. However, it is clear that there is no dramatic difference in the kinetics of all the systems under study. Moreover, as can be seen from Figure 4, the rate capability of Ca^{2+} and Mg^{2+} ions upon there insertion into V_2O_5 xerogel (composites with propylene carbonate[25] and carbon,[11] respectively) is very similar. This resemblance in the electrochemical performance for the two divalent cations and different designs seems to testify that these systems cannot be much further improved because they are close to optimum. To verify this conclusion, let us look more carefully into the mechanism of Mg insertion into such materials.

P. E. Tang et al. suggested that the materials based on V_2O_5 gels work as pseudocapacitors,[24] i.e., their electrochemical activity is related mainly to electro-adsorption at the surface. However, the attainment of the nearly theoretical capacity for V_2O_5 xerogels with relatively low surface area is evidence of regular intercalation (the specific capacity obtained with the high surface area supercapacitors is fundamentally lower than that of the intercalation compound). In the latter case, the shielding

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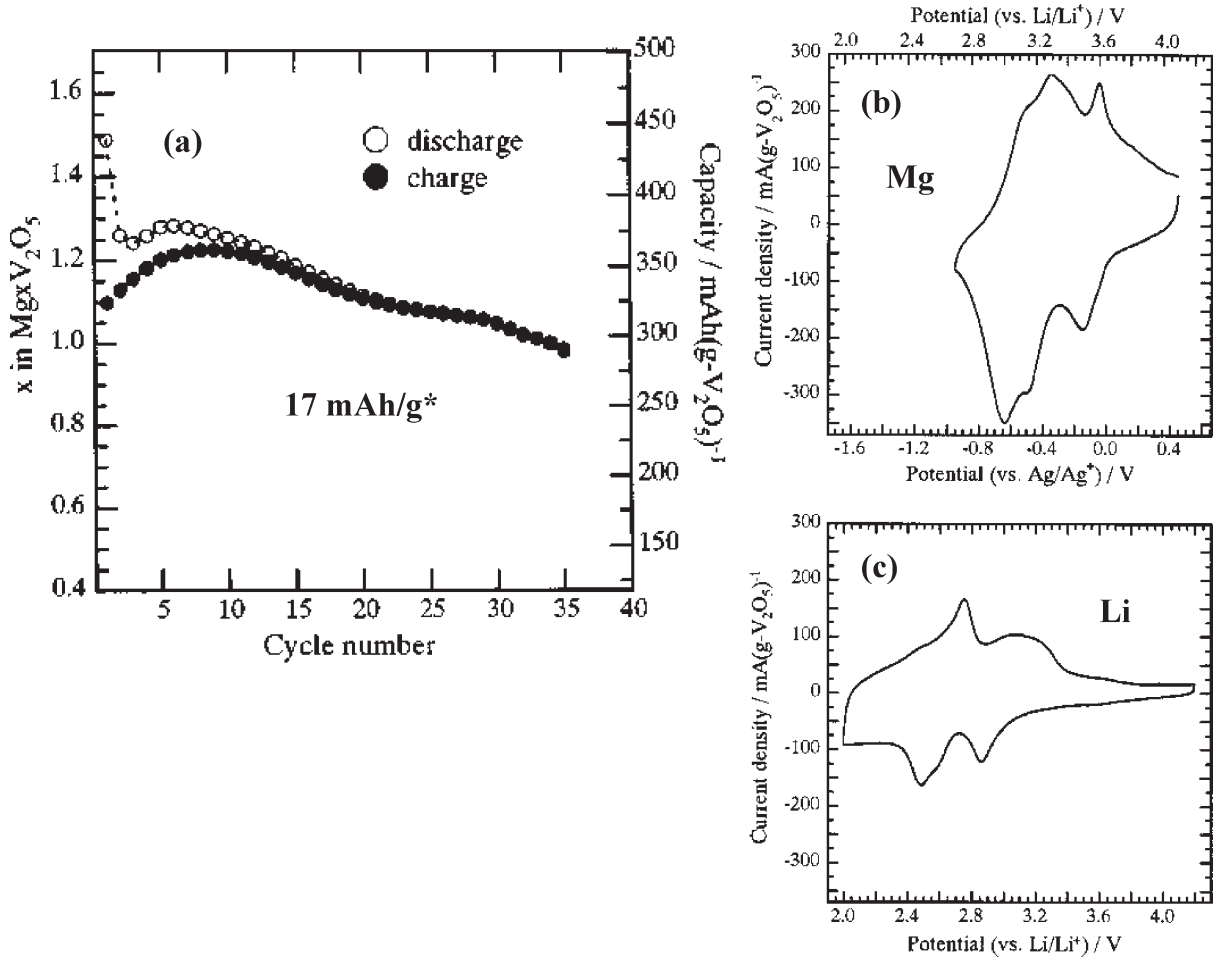

Figure 3. Electrochemical behavior of carbon particles covered by a thin layer of V_2O_5 xerogel: (a) capacity vs cycle number (a current density of 17 mA/g, *C*/40 rate, i.e., duration of one cycle is about 40 h); (b, c) cyclic voltammetry in the 1 M $Mg(ClO_4)_2$/acetonitrile and 1 M $LiClO_4$/propylene carbonate solutions, respectively (~1 mg V_2O_5, sweep rate of 0.1 mV/s), according to ref 11. We believe that a current density of 17 Ah/g presented in the original paper is an error. Reprinted with permission from ref 11. Copyright 2003 Electrochemical Society.

mechanism proposed by other researchers[23,26] seems to be more relevant. Actually, in spite of the deep drying at 100 °C, active materials based on V_2O_5 gels always contain a significant amount of structural water (about 0.4 mol of H_2O/mol of V_2O_5),[20] which seems to remain in the intercalation compound during cycling.[12] In addition to water, other polar molecules, such as acetone, acetonitrile, etc., can intercalate between the V_2O_5 bilayers, resulting in characteristic *d*-spacing of pillared nanocomposites.[20,26] Such intercalation may occur spontaneously during the material's preparation[27] or as a result of special efforts to design a new composite. For instance, it was shown[25] that the specific capacity of Ca insertion increases from 25 mA h/g in pure V_2O_5 xerogel to 280 mA h/g in its composite with propylene carbonate. However, the mechanism of the ionic transport in such hybrid compounds remains unclear because of insufficient knowledge of their atomic structure.

The latter is well-established for the V_2O_5 xerogel host, which is packed by the V_2O_5 bilayers,[28] but less is known regarding the guest cation sites and their environment inside the intercalation compounds. At first glance, the hybrids should be structurally similar to the products of the electrolyte cointercalation into microcrystalline V_2O_5 (Figure 2). In this case, the inserted cations should occupy exclusively the centers of the solvation shells, e.g., the oxygen octahedra formed by H_2O molecules. However, the high capacity of the hybrids suggests the existence of additional cation sites (shown in green in Figure 2) within the intercalated layers. In fact, such peripheral sites located close to the V cations (Cu−V distance is equal to ~2.8 Å) were discovered for the Cu-doped V_2O_5 gels (Figure 5).[29] The insertion of divalent cations into these sites should result in a relatively slow ionic transport, because they are not separated from the vanadium ions by solvation shells. Thus, the main kinetic problem of this type of intercalation compounds, which seems to be impossible to eliminate, is the insufficient charge screening for the inserted cations.

In spite of this, such hybrid compounds, where inorganic layers alternate with those of H_2O or other polar molecules, seems to be very attractive because of the strikingly high potentials found for Mg insertion in these materials. As was

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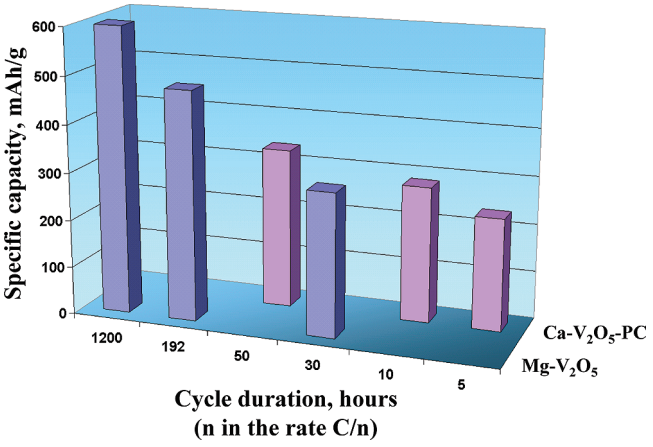

Figure 4. Rate capability of Ca^{2+} and Mg^{2+} ion insertion into V_2O_5 xerogel (composites with propylene carbonate and carbon, respectively) calculated on the basis of the data in refs 25 and 11, respectively. (Compare with theoretical capacity of V_2O_5 equal to 589 mA h/g).

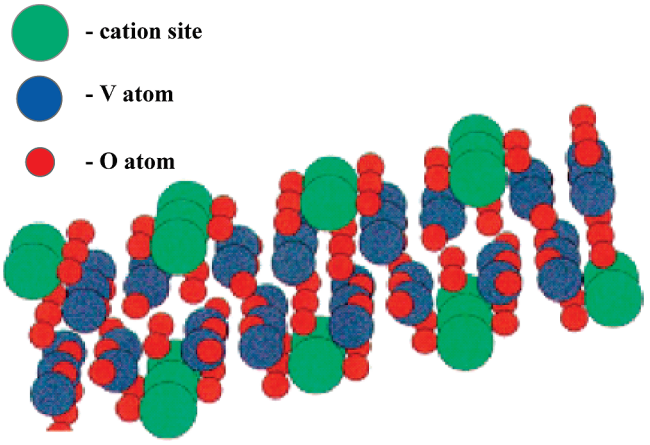

Figure 5. Cu cation location close to vanadium atoms in the copper-doped V_2O_5 aerogel according to ref 29. Reprinted with permission from ref 29. Copyright 2003 American Chemical Society.

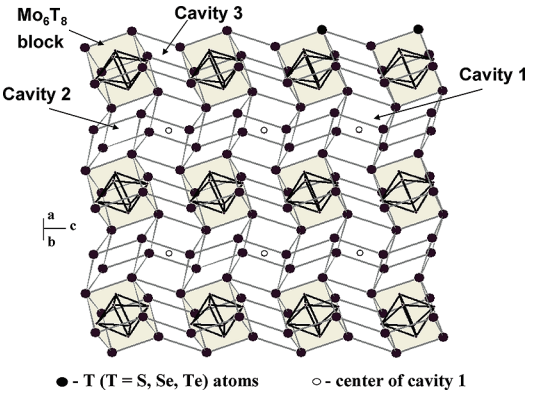

Figure 6. Crystal structure of Chevrel phases with Mo_6 clusters according to ref 40. Reprinted with permission from ref 40. Copyright 2006 American Chemical Society.

mentioned in the Introduction, the experimental data for the water-free systems, as well as simple estimations of potential energy of intercalation compounds, show that for the same host, the voltage of Mg insertion should be lower than that of Li insertion (compared to the same reference electrode). For TiS_2 and Mo_3T_4 (T = S, Se) this difference is equal to ~0.3 V.[4,10] However, for compounds based on V_2O_5 gels, Mg intercalation occurs at potentials even higher than those of Li.[1,11,12]

To explain this unusual phenomenon, let us describe, for simplicity, the hybrids with inserted Mg as the products of Mg−electrolyte cointercalation into a pure inorganic host. It is well-known that cointercalation occurs at potentials essentially higher than those for bare cation insertion. For instance, normal Li insertion into graphite begins at ~ 0.3 V, whereas its cointercalation with some organic electrolytes, such as dimethylsulfoxide, takes place[30] at potentials higher than 1 V because of the noncompensated solvation energy for this cation. Actually, in our calculations of the average voltage in common rechargeable Li (or Mg) battery (see eqs 1 and 2 in the Introduction), the cation solvation energy was not taken into account, because its changes at the anode and cathode sides were compensated (the energy needed for cation desolvation before its insertion into cathode material is equal to that of its solvation upon metal dissolution). In contrast, in the case of cation solvation inside the host (the case of cointercalation or insertion into hybrids), the ionic transport from the solution to the solid occurs without cation desolvation, or with only partial desolvation, and this energy gain increases the average working voltage of the battery. As the solvation energy of divalent Mg^{2+} cation (in simple salts, like $Mg(ClO_4)_2$ and triflate) is essentially higher than that of Li^+ in similar electrolyte, the potential of Mg insertion into the solvated host may be even higher than that of Li.

Cluster Compounds As Unique Hosts for Polyvalent Ion Insertion. As was mentioned in the Introduction, the slow kinetics of Mg solid-state diffusion is caused by the complexity in the redistribution of the bivalent cation charge within the local crystal structure of the inorganic hosts. This problem does not exist in Chevrel phases (CPs), Mo_6T_8 (T = S, Se) (Figure 6), where the Mo_6 clusters can easily exchange up to four electrons (Note that formal charge of individual Mo cation changes from $2\ ^2/_3$ to 2). As a result, the CPs enables the fast and reversible insertion of various cations, monovalent (Li^+, Na^+, Cu^+) as well as divalent Zn^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, and Mg^{2+} at ambient temperatures, which is also associated with the high electronic conductivity of the intercalation compounds.[14,31] Moreover, ternary CPs, $M'_yMo_6T_8$ ($M' = Na^+, Cu^+, Ag^+, Ni^{2+}, In^+, Fe^{2+}$, or Co^{2+}), can undergo reversible displacement reactions upon the insertion of cations, such as $M^{n+} = Li^+$, Na^+, Mg^{2+}, or Zn^{2+}:[31−33]

$$xM^{n+} + M'_yMo_6T_8 + 4e^- = M_xMo_6T_8 + yM'(\text{metal}) \quad (3)$$

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Such a reaction suggests a coupled M−M′ cations' motion in the crystal structure of the quaternary compounds, $M_xM'_yMo_6T_8$.

These unusual effects, discovered for the first time about 30 years ago, were explained[31] by quasi-monovalent state of these cations as transients, which results from a rapid one-electron transfer via the Mo_6T_8 matrix, e.g., $Zn^{2+} + e^- \leftrightarrow Zn^+$ (compare this explanation with our idea about the easy attainment of local electroneutrality by Mo_6 clusters). In addition, it was shown that the main parameter that affects the cation mobility in CPs is their size. However, the reason for the latter phenomenon was not discussed in detail. It was only mentioned that large cations (radius >1 Å) falls into a combined energetic/steric trap and block any ionic transport.[31] Most of the subsequent works were devoted to other attractive physical properties of CPs, e.g., electric, thermoelectric, magnetic, and catalytic. The recent application of Mo_6T_8 as unique cathodes for rechargeable Mg batteries[4] initiated our interest in studying the mechanism of cation mobility in CPs.

It was shown[3,4,34] that CPs do not need special nanoscale preparation to be used as practical Mg cathodes (Figures 7 and 8). Actually, for microcrystalline Cu-Mo_3S_4, a specific capacity of 102 mAh/g can be realized at the *C*/3 rate (a cycle of 3 h), while the theoretical capacity for this composition is equal to 120 mAh/g. For comparison, for composites based on the V_2O_5 gels, theoretical capacity of 589 mA h/g can be reached only at a *C*/1200 rate (a cycle of 1200 h). Mg/Mo_3S_4 prototype coin cells exhibited excellent cycling stability (more than 2500 cycles). Thus, the aim of the subsequent studies was to simplify the material preparation,[35,36] as well as to correlate the electrochemical performance to the composition,[3,32,37] morphology[3,38] and peculiarities of the CPs' crystal structure.[33,39−42] Comparative analysis[14] of the diffusion pathways for CPs with various cations based on their crystallography (mapping of all the cation sites, including the transport ones, as well as estimations of their potential energy according to the distances of these sites from adjacent anions and cations) allowed an understanding of the very complex transport phenomena in CPs such as: (i) the apparent immobility of the large M cations like Pb^{2+}, Sn^{2+}, Ag^+ in the ternary phases, MMo_6T_8; (ii) the coupled M + M′ diffusion in the quaternary phases, $M_xM'_yMo_6T_8$, where both large and small cations can assist; (iii) cation trapping in the Mg−Mo_6S_8, Cd−Mo_6S_8, and Na−Mo_6T_8 systems; (iv) a combination of low and high rate diffusion kinetics at the first and last intercalation stages, respectively, for the Cu−Mo_6S_8, Mn−Mo_6S_8, and Cd−Mo_6Se_8 systems; and (v) a fast ionic transport for small cations like Ni^{2+}, Zn^{2+}, and Li^+. It was shown that, in spite of the apparent ionic immobility for some compositions, the Mo_6 clusters in CPs ensure high diffusivity (at RT) for mono and divalent cations with a wide spectrum of sizes.[14] The CPs hosts have only one fundamental disadvantage: a low average voltage for Mg insertion, ~1.1 V vs Mg/Mg^{2+}.

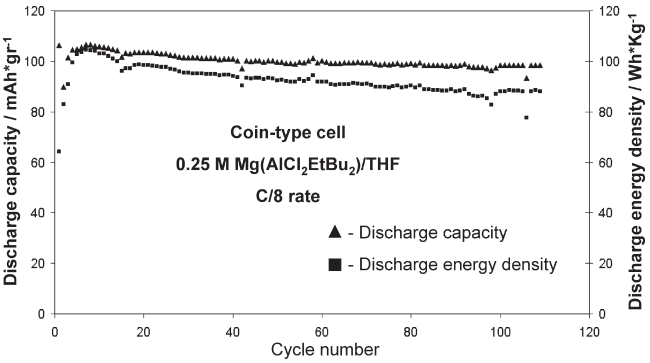

Figure 7. Discharge capacity and energy density of the Mg−Mo_6S_8 system vs cycle number (note that the charge of the cell includes an additional potentiostatic step at 1.8 V to decrease the cation trapping).

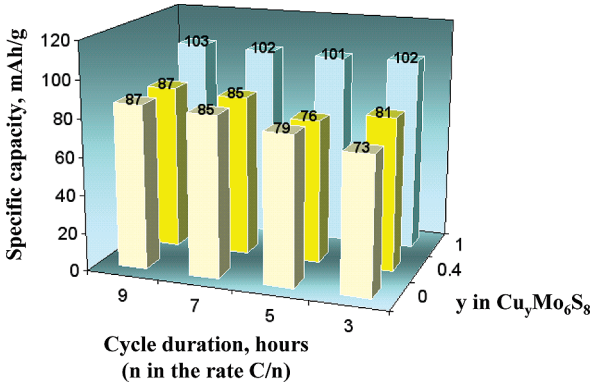

Figure 8. Rate capability of the Mg−$Cu_yMo_6S_8$ system without an additional potentiostatic step at 1.8 V. Compare with theoretical capacity of $Cu_yMo_6S_8$ equal to 129 and 120 mA h/g for $y = 0$ and 1, respectively.

Thus, it seems that future exploration for new cathode materials for rechargeable Mg batteries should be focused on cluster-containing intercalation compounds, exhibiting a higher capacity and working potential. For the moment, two directions for such development can be suggested.

(1) The study of Chevrel-type intercalation compounds such as $Mo_{15}T_{19}$ and Mo_6T_6. The crystal structure of these materials is also based on the Mo_6 clusters; in contrast to CPs, they are not isolated, but condensed.[43] Previously, it was shown[44,45] that these compounds are

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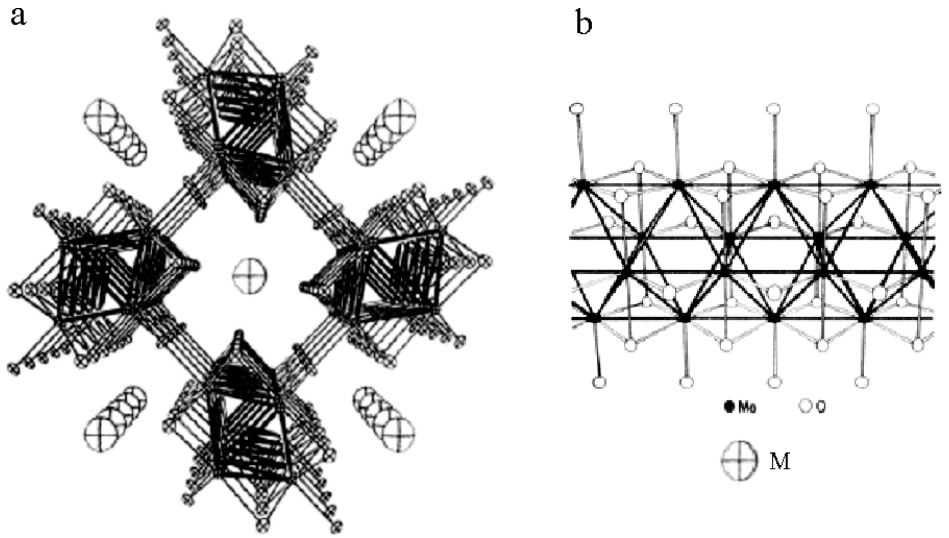

Figure 9. (a) Crystal structure of MMo_4O_6 (M = Na, K, Ca, Ba, In) compounds with infinite chains of edge-sharing Mo_6 octahedra. (b) One of the chains with oxygen coordination according to ref 49. Reprinted with permission from ref 49. Copyright 1983 American Chemical Society.

able to intercalate up to 7 and 9 Li^+ ions per formula unit, respectively. Moreover, a relatively fast and reversible intercalation of divalent cation (Cd^{2+}) was already demonstrated for Mo_6Se_6, Mo_9Se_{11}, and two different forms of $Mo_{15}Se_{19}$.[46] Even in the case that the electrochemical characteristics of the proposed new Mg hosts will be lower than that of CPs, their study should confirm the proposed diffusion mechanism and offer new challenges in the Mg cathode elaboration.

(2) The study of cluster-containing Mo oxides. Recently, a large number of cluster-containing Mo oxides have been synthesized.[47,48] In the literature, there is still no information about insertion reactions into such compounds, but according to the open crystal structure of $NaMo_4O_6$, $Sc_{0.75}Zn_{1.25}Mo_4O_7$, MMo_8O_{10} (M = Li, Zn), $Mn_{1.5}Mo_8O_{11}$, and $R_4Mo_4O_{11}$ (R = Nd−Lu, Y), intercalation activity can be expected. The basic structure of these compounds differs mostly by the coupling of the Mo_6 cluster chains (Figure 9)[49] to form the lattice. Replacement of the chalcogenides by oxides should increase the specific energy of the battery because of (i) the lower molecular weight expected for the host (due to the lower molecular weight of oxygen), and (ii) the higher electrochemical potentials of insertion reactions (as a result of the higher electron withdrawing power of oxygen). However, such replacement may result in diffusion complexities related to the higher ionicity of the chemical bonds in oxides as compared to chalcogenides.

We hope that new interesting intercalation compounds based, for instance, on Fe_6, Co_6 or Cr_6 clusters will be synthesized in future. Such compounds can be good candidates as Mg insertion materials.

It is obvious that any elaborate discussion regarding Mg cathodes cannot be completely separated from electrolytes issues. However, the main focus for the Special Issue is on solid-state materials chemistry, and thus expansion on electrolytes for Mg batteries is out of the scope for this paper. It is important, though, to emphasize that comprehensive studies are underway with various modifications of the organohaloaluminate based solutions with the goal of extending their electrochemical stability window and solutions safety. Interested readers are kindly referred to our published works ,regarding these aspects of electrolytic solutions.[50−53]

Conclusion

Magnesium electrochemistry suffers from several serious limitations, such as anode/electrolyte incompatibility, narrow electrochemical stability window of the electrolyte solutions, slow solid-state diffusion of Mg^{2+} cations and relatively low specific energy of Mg batteries. This paper analyzes three main strategies presented in the literature to improve the kinetics of Mg transport in relevant cathode materials, namely, to use (i) nanoscale materials; (ii) hydrates or similar intercalation compounds, where the oxygen of the H_2O molecules or other additional anions can screen the charge of the inserted cations; (iii) cluster-containing compounds with easy attainment of local electroneutrality. A combination of the first and second strategies in materials, such as V_2O_5 gels and their derivatives, can generate relatively high voltage and capacity, but their kinetics is insufficient for

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practical battery use because of the incomplete charge screening upon cation insertion. In contrast, cluster containing compounds like Chevrel phases show high rate capability and exclusively stable cycling, but low battery voltage. Thus, a future search for cathode materials for rechargeable Mg batteries should to be focused on new cluster-containing intercalation compounds with a higher working potential.

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