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*R.D. Apostolova, Yu.V. Polishchuk***MnO₂ POLYMORPHS IN MAGNESIUM BATTERY PROTOTYPE IN NON-AQUEOUS ELECTROLYTES: A MINI-REVIEW**

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In this article, the results of the research on MnO₂ polymorphs as suitable magnesium-inserting cathodic material for the secondary high energy magnesium batteries are critically reviewed. It is shown that MnO₂ magnesianation differs from classic type of Li intercalation. Magnesianation of MnO₂ can proceed by intercalation or conversion. Conversion with quick loss of the discharge capacity at cycling in «dry» non-aqueous electrolytes is observed in most of MnO₂ polymorphs (α -, δ -, closed to γ - phases and OMS-5). Intercalation is more probable in spinel phase. The lack of the electrolyte suitable for effective MnO₂ magnesianation is one of the major issues affecting successful realization of high energy Mg battery. Another challenge is slow Mg²⁺ diffusion in the cathodic host. Water addition to «dry» electrolyte improves MnO₂ magnesianation. In this case, magnesianation proceeds through an intercalation-type reaction. However, the water is incompatible with Mg anode. New strategy for increase of the Mg²⁺ mobility is required. Dual Mg/Li electrolyte and some proposed solutions that could be successful strategies for further development of high energy magnesium batteries are presented.

Keywords: MnO₂ polymorphs, Mg battery, diffusion, Mg oxide film, cyclic efficiency, dual-ion electrolyte, intercalation, conversion.

Lithium-ion batteries (LIB), known as the leading power sources for portable electronic devices (notebook, mobile telephone, etc.) and the micro mechanisms (smart cards, etc.) [1], do not satisfy current needs of superior energy consumers (electric vehicles, grid storage, etc.) for power, safety and cost. Magnesium batteries (MB) can be available alternative of LIB [2–8] because of magnesium merits. Magnesium is cheaper than lithium; its specific volume capacity (3833 mA·h/cm³) is two times more than that of lithium; the dendrites do not grow on the magnesium surface whereas their formation on lithium can lead to the short circuit in battery and ecological catastrophes; magnesium can be reversibly deposited/dissolved in magnesium electrolytes; magnesium is widespread in nature.

However, the implementation of the concept of Mg-intercalation similar to lithium is now ineffective. Harmful oxide film on magnesium surface is a difficult problem to solve. The slow diffusion of divalent Mg ions in cathodic host is another challenge for the implementation of Mg battery.

The first magnesium battery prototype on the basis of Mo₆S₈ Chevrel phase cathode was proposed by Aurbach et al. [9]. Discharge characteristics of

the prototype (average voltage $E_{\text{disch}}=1.1-1.2$ V and capacity $Q_{\text{disch}}=110-120$ mA·h/g) are not equal to those of commercial LiCoO₂/graphite LIB with parameters of $E_{\text{disch}}\sim 3.7$ V and $Q_{\text{disch}}=140$ mA·h/g. Two structures of spinel and layer TiS₂ showed satisfactory magnesianation with Mg anode after discovery of the first cathodic magnesium insertion material of Mo₆S₈ [10,11]. Their weak interaction with Mg²⁺ ensures sufficient Mg²⁺ mobility in the cathodic host but voltage and capacity of MB are insufficient for their substitution of LIB.

The practical energy of MB can be improved through the use of two strategies: (1) low voltage of MB can be compensated by high discharge capacity (if discharge capacity is increased to $Q_d=300$ mA·h/g, adequate discharge voltage of MB should reach 2.0 V); and (2) the discharge voltage of MB can be increased through the use of redox couples of Co³⁺/Co⁴⁺ and Ni³⁺/Ni⁴⁺. The systems ensure successfully discharge capacity of LIB in 5 Volt configurations. However, magnesium electrolyte with wide windows of electrochemical stability that is appropriated for using the redox couples does not exist.

The material for positive electrodes with high

redox potential, high capacity and the Coulomb efficiency at a long cycling is required for substitution of LIB by MB. Numerous chemical compounds were tested in magnesium battery prototype with the intention to achieve energy characteristics of LIB: C_{60} , Mo_9Se_{11} , $\alpha-MnO_2$, $\alpha-MnO_2/C$, $\lambda-MnO_2$ spinel, V_2O_5/C , Co_3O_4 , RuO_2 , MoO_3 , $MgCoSiO_4$, $Mg_{1.03}Mn_{0.97}SiO_4$, $MgFeSiO_4$, $MgFePO_4F$, MoS_2 , S, S/C composition, $AgCl$, $FeOCl$, TiS_2 , $NiHCF(H_2O)$, $VOPO_4$, etc.

The best discharge characteristics were obtained with magnesium polyanions. The discharge capacity of { $MgFeSiO_4/0.5$ mol/L Mg-tri-fluoromethylsulfonil imide (TFSI) $_2$, acetonitrile/Mg} system reaches 330 mA·h/g at the discharge voltage of 2.2 V, but it was shown only for 5 cycles [12]. Thus, the lack of appropriate cathode that provides high-energy density and good sustainability greatly hinders the development of practicable MB. A challenge to find suitable MB cathode is widely believed to be a consequence of bivalency of Mg^{2+} [4,13]. High density of Mg^{2+} charge reduces the mobility of Mg^{2+} because of Mg ion interaction with ion environment in the cathodic host and also generates other undesirable effects.

Cathodes based on oxides of MnO_2 , V_2O_5 and MoO_3 generally have high voltages and their reversible magnesiation was shown. The stagnation mobility of multivalent ions is observed in metal-oxide structures. However, metal oxides are still of great interest because of their high potentials [14–25].

MnO_2 dioxide attracts special attention due to its low cost, high safety, the abundance in nature and also because of high theoretical voltage (~2.8 V). The theoretical capacity of MnO_2 -compounds in redox reaction with magnesium is equal to 308 mA·h/g for inserting ~0.5 mol or 1 equivalent of Mg, leading to desirable energy densities of ~862 W·h/kg and ~3630 W·h/L [6].

MnO_2 has many structural polymorphic forms, including several open channel structures (α -phase: 2×2 channel; β -phase: 1×1 channel; γ -phase: 1×2 channel), layered δ -phase and spinel phase. These phases have been found suitable for the insertion of various cations with different sizes. The twisted MnO_6 octahedrons make double chains with one-dimensional channel in the channel structures of MnO_2 . The profile of the channel depends on the number of octahedrons which surround the channel. Three dimensional lattice paths exist in the structure of spinel phase where cations migrate between octahedral and tetrahedral sites.

The electrochemical intercalation of Li^+ into MnO_2 compositions was investigated earlier than that

of Mg^{2+} [27–30]. The chemical insertion of Mg^{2+} into different MnO_2 -phases was investigated by Bruce et al. [31]. The electrochemical magnesiation in MnO_2 polymorphs has attracted much attention recently [32].

The intercalation mechanism of magnesiation was proposed as a prototype of lithium intercalation conception in the early stage of magnesiation investigations. The analysis of research results of MnO_2 magnesiation requires the transformation of the conception. It was determined that magnesiation differs significantly from classic type of lithiation. Magnesiation in MnO_2 polymorphs can proceed by the intercalation or conversion. The comparison of the intercalation and conversion during magnesiation of MnO_2 was performed in work [14].

To understand the reaction mechanism between $\alpha-MnO_2$ and Mg^{2+} , advanced analysis of the discharge product was carried out [33]. An amorphous layer was discovered on the surface of $\alpha-MnO_2$ while the core still remained crystalline. The amorphous shell consists of reduced Mn^{3+} , Mn^{2+} and Mg^{2+} species. Impedance research results show increasing resistance of charge transfer through amorphous surface layer on MnO_2 [34]. However, its contribution to the electrode processes is negligible due to minor value of film thickness (1 nm) as compared with the contribution of Mn-dissolution and the decomposition of the electrolyte.

It was found that the surface area of MnO_2 cathode significantly affected the initial discharge capacity. Below 60 m²/g, the initial discharge capacity rapidly increased with surface area. Above this value, the initial discharge capacity remained constant. This trend was not affected by the exact polymorphism and chemical composition of MnO_2 . The fact that the magnesiation process was mainly controlled by the surface of MnO_2 is consistent with the conclusion: the magnesiation of MnO_2 is unlikely to occur via the intercalation of Mg^{2+} . The thermodynamic driving force for the conversion reaction is attributed to the high stability of formed MgO oxide.

α -, β -, γ - and δ -phases of MnO_2 show uniform discharge-charge behavior at magnesiation with rapid capacity loss to 50–60 mA·h/g at cycling, pointing out conversion reformation [14,35,36]. The appreciable difference of discharge capacity in polymorphs with different structures was not observed. It was shown that tunnel size does not influence the start discharge capacity. It means that the volume diffusion does not influence discharge capacity. Downward change of the voltage profile at magnesiation of MnO_2 phases is typical. Octahedral molecular sieves (OMS-5 phase of MnO_2 with 4×2

channel) also have a downward profile of the voltage [37]. Downward profile refers to the formation of solid solution, pseudo-capacity or conversion behavior. It was assumed that the availability of volume structure spaces may facilitate Mg^{2+} diffusion. However, the potential possibility of conversion reactions is the process which results in irreversible formation of persistent MgO substance.

The proposed conversion mechanism obeys the following scheme:



Conversion reaction forms MgO, MnO and Mn_2O_3 oxides.

The classic intercalation forms the different structures of Mg_xMnO_2 as follows:



It is assumed that there is the possibility of two paths in one polymorph at the different early stages of magnesianation. On the other hand, magnesium intercalation was observed in λ - MnO_2 spinel in aqueous solutions [5].

Unlike lithium intercalation, where solid state interface on Li is permeable for Li ion, the oxide film on magnesium blocks the transport of Mg^{2+} in conventional electrolytes used for lithiation and also in the majority of new electrolytes for magnesianation. A substantial density of divalent Mg ions charges promotes their slow mobility in ion environment of MnO_2 host because of intense electrostatic interaction. It is related to slow kinetics of the MnO_2 polymorph magnesianation.

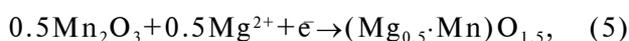
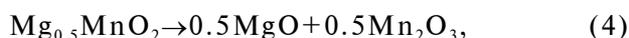
The average discharge voltage of MnO_2 /Mg accumulator prototypes is low. It is frequently within the limits between 1.4 V and 1.6 V, which is lower than the discharge voltage of MnO_2 /Li system (\sim 2.8 V).

The effective transformation of magnesium battery depends on the compatibility of the cathode, anode, electrolyte and battery construction materials. A numbers of Mg electrolytes exhibit the compatibility with Mg anode and high stability. Now, there is no information about the electrolyte that can be appropriated for MnO_2 magnesianation with high Coulomb efficiency at long cycling [5]. The lack of cathodic materials with effective Mg^{2+} insertion capability and high operating voltage is one of the challenges facing the implementation of high energy Mg batteries.

Comparative estimation of magnesianation of

MnO_2 polymorphs with different structure was accomplished in work [15]. There are ramsdelite R (close to γ - MnO_2), $MgMn_2O_4$ (close to $CaFe_2O_4$ with triangle channel) named CF, gollandite (α - MnO_2) and spinel phase. The instability of intermediate electrode products displayed intercalation way of conversion in α - MnO_2 [6]. Spinel has a tendency toward intercalation. According to thermodynamic data, the products of magnesium intercalation of α -, R- and CF-phases are not stable with the exception of intermediate products of spinel phase. It was shown that a-axis expands and b-axis reduces in crystal lattice of α - MnO_2 at the insertion of magnesium ions (when $x > 0.125$ in Mg_xMnO_2). The average parameter of MnO_2 deformation after intercalation increases by two orders of magnitude because of Jahn-Teller defect. The volume expansion of R- MnO_2 for $Mg_{0.5}MnO_2$ reaches 21.4% which is related to the unsatisfactory reversible intercalation. The classic type of Li^+ intercalation was reconsidered for magnesium type in dry organic electrolyte systems on the basis of obtained magnesianation results.

It was assumed that there is the possibility of the electrochemical and chemical transformations in conversion MnO_2 magnesianation processes as follows [33]:



Strong affinity between Mg and O stabilizes exceedingly MgO structure. The magnesium conversion, which forms the stable MgO structure, has much higher potential than that of lithium.

The first-principles calculations show that Mg^{2+} diffusion mainly depends on the change of coordination around multivalent ions [26,38].

The capacity of MnO_2 magnesianation can be increased to 150–230 mA·h/g at the voltage of 2.6–2.8 V during long cycling exceeding 100 cycles [39,40]. Such enhanced results were obtained in the systems with different amount of water additions. The water in the structure of the oxide or in the electrolyte containing acetonitrile, $Mg(ClO_4)_2$ or diglym, $Mg(TFSI)_2$ improves the slow kinetics of Mg^{2+} in the oxide space, screening Mg^{2+} charge. Two useful functions of water were proposed: the decrease of the activation energy of Mg^{2+} desolvation

and the formation of hydrated magnesium ions $\text{Mg}^{2+}(\text{H}_2\text{O})_n$. The general quantity of water is an important factor but the adjustment of an optimal ratio $\text{H}_2\text{O}/\text{Mg}^{2+}$ is necessary. This was shown in the systems of amorphous porous nanometer MnO_2 , $\text{Mg}(\text{ClO}_4)_2$, propylene carbonate [41] and V_2O_5 , $\text{Mg}(\text{ClO}_4)_2$, acetonitrile [42]. Thus, reversible Mg^{2+} intercalation may be possible in $\delta\text{-MnO}_2$ in the electrolytes with water addition. However, the activation of magnesiation by water faces a problem. Water can passivate Mg electrode, evoke dissolution of Mn from MnO_2 oxide in the electrolyte and provide other parasitic reactions. In addition, high start discharge capacity at $x > 0.5$ in Mg_xMnO_2 [36,43] may rise because of the decomposition of the electrolyte due to the low anodic stability of most Mg electrolyte (~ 3.5 V) [44].

It was proposed that the co-intercalation of Mg^{2+} and water causes the structure ionic blend and the structure reorganization of MnO_2 at the discharge extraction of water; Sun et al. [40] observed an appreciable contraction of MnO_2 interlayer space.

The effects of water on the conductivity, viscous and IR spectra of the electrolytes for the batteries on the basis of Mg, Na, and Li were investigated in work [45]. The formation of ion-solvent and ion-ion associations was determined. The change of ClO_4^- -solvent bonds that was evoked by water addition indicates the formation of contact ion pairs. The appearance of the intensive non-active bond at 934 cm^{-1} in IR spectra in the presence of water was related to cation- $\text{H}_2\text{O}-\text{ClO}_4^-$ pairs.

The role of water addition in ionic liquids (IL) was investigated using organic additions (ethylene glycol, toluene, tetrahydrofuran, dimethylsulfoxide) [46]. Satisfactory discharge characteristics were obtained in the Mg/air system with ionic liquid of Mg-(tri-ethyl-tetradecyl-phosphonium chloride) with ethylene glycol. The improvement of the characteristics was explained by the following positive effects: (1) the decrease of electrolyte viscous, (2) the formation of Mg^{2+} -conductive film on magnesium surface as the result of the interaction of Mg^{2+} with addition, and (3) the participation of protons in the electrode processes.

The success of hybrid non-aqueous electrolyte is especially necessary to note [47]. Here, the window of the electrochemical stability of the electrolyte is equal to 3.8 V vs. Mg/Mg^{2+} . The hybrid electrolytes were developed on the basis of (TFSI)-sols: $\text{Mg}(\text{TFSI})_2\text{-LiTFSI}$ and $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2\text{-LiTFSI}$ in glyme solvents. LiMn_2O_4 , LiCoO_2 or $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ on Al-current collector was used in positive electrodes and Mg was used as a negative electrode. The start

discharge capacity Q_1 of $\text{Mg}/\text{LiMn}_2\text{O}_4$ system reaches 106 mA·h/g, in the second cycle $Q_2=102$ mA·h/g, and in the 40th cycle $Q_{40}=53$ mA·h/g at the voltage of 2.8 V. These hybrid electrolytes are capable of reversible deposition/dissolution of magnesium on aluminum. Li-intercalation dominates on the cathode and reversible deposition of Mg occurs on the anode in Li-Mg hybrid electrolytes. Dual electrolytes on the basis of $\text{Mg}(\text{TFSI})_2$ and $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in glyme solvents are barely free from Cl^- -ions which exert negative influence on the corrosive stability of construction materials of the magnesium batteries. The conductivity of 0.5 M $\text{Mg}(\text{TFSI})_2\text{-LiTFSI}$ /diglyme electrolyte is equal to 4.13 mS/cm at 20°C.

The possibility of Li/oxychloride substitution for $\text{Mg}/(\text{MnO}_2$ or $\text{MoO}_3)$ was considered in MaxPower, Inc. [48]. The system on the basis of MoO_3 in bipolar packing with Mg plate was elaborated in D-cell configuration. Its energy is equal to 9.8 W·h. The comparable energy of MnO_2/Li D-cell produced by Soft Company is three times as much (29 W·h).

Peculiarities of $\alpha\text{-MnO}_2$ and tunnel OMS-5 magnesiation

The effective reversible magnesiation of $\alpha\text{-MnO}_2$ and tunnel OMS-5 polymorphs is associated with the problem of essential capacity loss at cycling (50% of start discharge capacity) [36,37]. The loss can be caused by the formation of MgO in conversion reaction [14,33,35] and also the dissolution of Mn in the electrolyte with its further deposition on anode [33,36,49]. Arthur et al. experimentally confirmed the formation of MnO, Mn_2O_3 and MgO after magnesiation of $\alpha\text{-MnO}_2$ [14,33,35]. The formation of MgO and MnO insulators blocks the reversibility and cycle life of the battery prototype limits.

Tutusang et al. tested coin cell containing $\alpha\text{-MnO}_2$ on stainless steel/Mg system in boron-cluster electrolyte of 0.75 mol/L $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in tetrahydrofuran [50]. As a result, 10 stable charge-discharge cycles was obtained. It was admitted as a certain achievement in the development of high voltage MB.

The nanostructured MnO_2 conversion-based electrodes are useful for the improvement of the electrode kinetics [35].

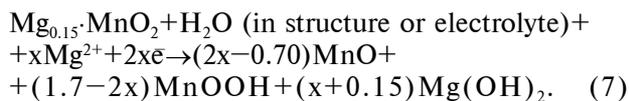
Peculiarities of $\delta\text{-MnO}_2$ magnesiation

Mg^{2+} intercalation in birnessite or $\delta\text{-MnO}_2$ dehydrated layer polymorphs has attracted the attention in works by Nam et al. [39] and Sun et al. [40] because of its better cycling in aqueous electrolytes in comparison with that in non-aqueous electrolytes. Water presence in the structure of MnO_2 and/or in the electrolyte can improve slow

intercalation kinetics of Mg^{2+} in MnO_2 screening Mg^{2+} charge by the water molecules with decreasing of the desolvation energy at deintercalation [33,40, 41,48,51].

Magnesiumation of $\delta\text{-MnO}_2$ was investigated by Nam et al. [39] in two electrolytes of $\text{Mg}(\text{ClO}_4)_2$, acetonitrile, H_2O and aqueous electrolytes. Reversible Mg^{2+} -intercalation (more than 10000 cycles at $\sim 50\%$ start capacity) and increasing capacity in aqueous electrolyte were shown at a voltage of ~ 2.8 V. It was impossible to exclude Mg^{2+} rise cycling ability by the participation of proton intercalation. Intercalation in layered $\text{Mg}_{0.15}\text{MnO}_2 \cdot 9\text{H}_2\text{O}$ was investigated by Sun et al. [40] using Ag/Ag^+ reference electrode and Pt counter electrode in the electrolyte of $\text{Mg}(\text{ClO}_4)_2/0.5$ mol/L H_2O . Start discharge capacity ~ 157 mA·h/g decreased after 20 cycles, which is contrary to the results of work [16]. Sun et al. declared about conversion reactions with surface formation of MnO and hydroxides on the data of X-ray photoelectron spectroscopy.

The participation of water in the following electrode reaction is assumed [52]:



Magnesiumation in $\delta\text{-MnO}_2$ in non-aqueous electrolytes is varied. Whereas Nam et al. [39] showed the reversible magnesiumation in the electrolyte on the basis of acetonitrile, Sun et al. declared about Mg^{2+} electrochemical cycling in the electrolyte of 0.25 mol/L $\text{Mg}(\text{TFSI})_2$, diglym only after long conditioning of the electrolyte.

Peculiarities of spinel structures magnesiumation

The insertion of Mg^{2+} into Mn_2O_4 spinel (known as $\lambda\text{-MnO}_2$) is evaluated by the theoretic capacity of 308.3 mA·h/g at ~ 2.9 V [26]. Determined energy migration barrier of Mg^{2+} ($\sim 500\text{--}800$ meV) assumes slow Mg^{2+} mobility in spinel oxide [26,38].

The reversible electrochemical behavior of MgMn_2O_4 spinel was shown by Sinha et al. in aqueous $\text{Mg}(\text{NO}_3)_2$ electrolytes during 20 cycles with non-high intercalation level ~ 35 mA·h/g [53].

Yuan et al. declared about electrochemical cycling Mg^{2+} and Zn^{2+} in $\lambda\text{-MnO}_2$ spinel in aqueous electrolyte [43]. Start capacity 545 mA·h/g is more than the theoretic value.

Kim et al. observed reversible electrochemical magnesiumation of MnO_2 spinel in aqueous solution of $\text{Mg}(\text{NO}_3)_2$ [54]. Less essential degree of magnesiumation was obtained in dry organic electrolyte of $\text{Mg}(\text{TFSI})_2$, diglym (3 at.% Mg/MnO_2) in relation to that in

aqueous electrolyte ($\sim 11\%$ at.% Mg/MnO_2).

Cabello et al. electrochemically demagnesiates tetrahedral MgMn_2O_4 spinel in aqueous electrolyte of $\text{Mg}(\text{NO}_3)_2$ using Ag/Ag^+ reference electrode and Pt counter electrode. Start discharge capacity reached 150 mA·h/g and was equal to ~ 100 mA·h/g at the 20th cycle [55].

Magnesium oxide and sulfide spinels attract the attention as cathodic and electrolyte materials of MB. The influence of inverse spinel on Mg^{2+} mobility in MgMn_2O_4 spinel as cathodic prototype and in MnIn_2S_4 as potential solid electrolyte was analyzed using the first-principles calculations [56]. It was determined that inverse spinel and the change of local environment contribute to a change of Mg^{2+} migration barrier in the oxides and sulfides. The inverse of the spinel is main limiting factor of the effective transformation of Mg spinel. The synthesis technology or the composition that stabilizes a spinel structure is critical factor for successful implementation of Mg spinel based batteries.

The capacity of $\lambda\text{-MnO}_2$ spinel equals about 100 mA·h/g at start discharge voltage of 1.7–1.8 V in the electrolyte of $\text{Mg}(\text{ClO}_4)_2$ 0.25 mol/L; ethyl methyl carbonate; γ -butyrolactone; and butyl-3 methyl-imidazolium-hexa-fluorophosphate (BMIPF_6). The addition of ionic liquid BMIPF_6 (5%) doubles average discharge voltage and the capacity of the system.

The critical analysis of the literature data about the reversible magnesiumation in the different MnO_2 polymorphs was provided in study [7]. Latest achievements concerning the activity of MnO_2 in Mg-power sources prototype were presented in works [18,44].

Conclusions

The analysis of the scientific literature on the state of electrochemical MnO_2 magnesiumation revealed that the interest in magnesium/ MnO_2 battery has increased over the past three years. The number of theoretical studies has increased too. It was shown that magnesiumation essentially differs from classic type of lithium intercalation. Magnesiumation of MnO_2 can proceed by intercalation or conversion. It depends on the type of MnO_2 polymorphs. Conversion with quick capacity loss at cycling was assumed in α -, δ -, ramsdelite-phases of MnO_2 . The intercalation of Mg^{2+} in spinel $\lambda\text{-MnO}_2$ is more probable. The possibility of two magnesiumation ways in the different stages of magnesiumation in one polymorph is assumed.

Surface oxide film on magnesium surface blocks the transport of Mg^{2+} in classic electrolytes used at lithiation and also in majority of new electrolytes used for magnesiumation. It is contrary to lithiation

where solid state interface on lithium is permeable for Li^+ . Considerable charge density of divalent guest Mg ions causes their slow mobility in ion environment of MnO_2 host because of the electrostatic interaction. As a result, the kinetics of magnesiation of MnO_2 polymorphs decelerates.

Average discharge voltage of MnO_2 polymorphs/Mg systems is low. It is equal to 1.4–1.6 V in dry aprotic electrolytes which is lower than discharge voltage of MnO_2/Li system (~2.8 V).

Now, the electrolyte which can be used for long effective transformation of MnO_2 in redox reaction with magnesium is not known. The electrolyte with high anode stability (3.8 V vs. Mg^{2+}/Mg) on the basis of magnesium sol with carborane-ion ($\text{CB}_{11}\text{H}_{12}$) combined with magnesium anode have been recently proposed. The electrolyte is recommended for high voltage cathodes of MB [57]. However, high potential of electrolyte anode stability does not guarantee the practical MnO_2 magnesiation because of unforeseen MnO_2 behavior under the influence of other factors (instability of intermediated products of electrode reaction, parasitic surface processes, etc.).

The recent theoretical and experimental investigations showed that spinel oxides present the promising group of Mg-cathodic materials [58].

Hybrid Mg/Li batteries deserve special attention. The successful demonstration of Mg/Li hybrid system of $\text{Mo}_6\text{S}_8/\text{magnesium electrolyte} + \text{LiCl}/\text{Mg}$ shows that the combination of Mg anode with Li-ion intercalation cathode can ensure a high rate of transformation along with high level of ecological safety. In addition, it can provide high Coulomb efficiency of MB [59].

The possibility of MnO_2 magnesiation in the electrolytes with water addition was shown. However, water activation of MnO_2 magnesiation causes the problem which needs to be addressed.

It is advisable to devote additional attention to researches of MnO_2 cathodic materials, the modification of the cathodic surface, dual ion electrolyte, and finding the protecting layer on Mg surface with following utilization of the modified Mg anode in the conventional electrolytes in conjugation with high voltage cathode. In conversion-based MnO_2 phases the discharge capacity depends on surface area. The optimization of their morphology and the particle sizes could be useful for the full utilization of the surface capacity. The proposed interlayer expansion in layered MoS_2 for the improvement of Mg^{2+} mobility could be applied to layered MnO_2 phase [60].

For practical magnesiation of MnO_2 , it is

necessary to minimize the structure deformation of MnO_2 oxide, improve the stability of intermediate intercalation products, and increase the mobility of Mg ions.

The battery Mn_3O_4 spinel/Mg, where the capacity originates from capacitive processes and the interfacial reactions are governed by the electrolyte solvent, has been presented [61]. The behavior observed for the Mn_3O_4 in APC (all phenyl complex)-DME electrolyte with a wide plateau around 0.2 V indicates that the material may be promising for use as anode in an Mg battery. The Mn_3O_4 nanoparticles were cycled with a reversible capacity of ~1800 mA·h/g at 15.4 mA/g. The extremely high capacity, together with the stable cycling performance (86% retention after the initial 200 cycles at 770 mA/g), represents a possibility to develop this new type of Mg battery with high charge storage performance as a substitute for intercalation based Mg batteries. In light of this work, utilization and development of the interfacial charge storage mechanism could be an effective strategy to enhance the electrochemical performance of Mg batteries.

In spite of certain success in the development of MB, necessary magnesium battery for substitution of LIB is now in its infancy in the opinion of the researchers elaborating MB.

Practical implementation of divalent batteries has been delayed. It depends on the topology discovery of host structure that controls quick mobility of divalent ions more than all other factors. The quest for suitable material for positive electrodes in MB is inseparable from the quest for suitable electrolyte for the material.

The question «Can multielectron intercalation reactions be the basis of next generation batteries?» [62] was answered as follows: (1) these reactions can occur in soft lattices, where the ionic charges are shielded from the highly charged Mg ion; (2) the spinel-type lattice appears to be preferred over layered structures; (3) there is no experimental evidence yet that more than a one electron reaction can be achieved in a magnesium intercalation reaction; (4) there is a deficit of around 0.5 V versus lithium cells. Thus, the question remains unanswered as to whether any magnesium based intercalation chemistry with a high free energy of reaction, average of 3 V for a two-electron reaction, can be made to be reversible at an acceptable rate of reaction while maintaining its structure. The theory would predict that magnesium-based intercalation cells are not a viable electrochemical option, relative to lithium cells, from either power or energy density considerations.

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MnO₂ ПОЛІМОРФИ У ПРОТОТИПІ МАГНІЄВОЇ БАТАРЕЇ У НЕВОДНИХ ЕЛЕКТРОЛІТАХ: КОРОТКИЙ ОГЛЯД

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Проведено критичний огляд результатів дослідження MnO_2 як можливого катодного матеріалу включення для вторинних високоенергоємких магнієвих батарей. Показано, що магнезування MnO_2 відрізняється від класичного типу інтеркаляції літію. Магнезування MnO_2 може відбуватися інтеркаляційним і конверсійним шляхами. Конверсія зі швидкою втраченою розрядної ємності при циклуванні в «сухих» неводних електролітах спостерігається у більшості поліморфів MnO_2 (α -, δ -, γ -фазах і OMS-5). Інтеркаляція більш імовірна у шпінельній фазі. Відсутність електроліту, підходящого для ефективного магнезування MnO_2 являється однією із перешкод для реалізації високоенергоємких магнієвих батарей. Іншою причиною є повільна дифузія Mg^{2+} у катоді-«хазяїні». Магнезування покращується при додаванні води у сухий електроліт. У такому разі, магнезування реалізується інтеркаляційним шляхом. Однак, вода не сумісна з Mg анодом. Необхідна нова стратегія для покращення рухомості іона Mg^{2+} . Для подальшого розвинення високоенергоємких магнієвих батарей перспективними стратегіями може бути використання гібридного Mg/Li електроліту і різні представлені у обзорі рішення.

Ключові слова: MnO_2 поліморфи, Mg батарея, Mg^{2+} -дифузія, Mg оксидна плівка, ефективність циклування, подвійний Mg/Li електроліт, інтеркаляція, конверсія.

MnO₂ POLYMORPHS IN MAGNESIUM BATTERY PROTOTYPE IN NON-AQUEOUS ELECTROLYTES: A MINI-REVIEW

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In this article, the results of the research on MnO_2 polymorphs as suitable magnesium-inserting cathodic material for the secondary high energy magnesium batteries are critically reviewed. It is shown that MnO_2 magnesiation differs from classic type of Li intercalation. Magnesiation of MnO_2 can proceed by intercalation or conversion. Conversion with quick loss of the discharge capacity at cycling in «dry» non-aqueous electrolytes is observed in most of MnO_2 polymorphs (α -, δ -, closed to γ - phases and OMS-5). Intercalation is more probable in spinel phase. The lack of the electrolyte suitable for effective MnO_2 magnesiation is one of the major issues affecting successful realization of high energy Mg battery. Another challenge is slow Mg^{2+} diffusion in the cathodic host. Water addition to «dry» electrolyte improves MnO_2 magnesiation. In this case, magnesiation proceeds through an intercalation-type reaction. However, the water is incompatible with Mg anode. New strategy for increase of the Mg^{2+} mobility is required. Dual Mg/Li electrolyte and some proposed solutions that could be successful strategies for further development of high energy magnesium batteries are presented.

Keywords: MnO_2 polymorphs; Mg battery; diffusion; Mg oxide film; cyclic efficiency; dual-ion electrolyte; intercalation; conversion.

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