



How solution chemistry affects the electrochemical behavior of cathodes for Mg batteries, a classical electroanalytical study

Ran Attias^{*}, Shaul Bublil, Michael Salama, Yosef Goffer, Doron Aurbach

Department of Chemistry, Institute of Nano-Technology and Advanced Materials (BINA), Bar-Ilan University, Ramat Gan, 5290002, Israel

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ABSTRACT

Mo₆S₈ Chevrel phase (CP) is still the most effective magnesium ions insertion material that was examined in cathodes for rechargeable Mg battery model systems. Its synthesis includes CuMo₆S₈ as an intermediate which undergoes Cu ions leaching. Thereby, CP materials may contain small amounts of copper. Cu_xMo₆S₈ undergoes complex magnesium insertion processes that include reversible displacement of copper. We report herein on a study of Cu_{0.09}Mo₆S₈ electrodes in two electrolyte solutions which are important for secondary Mg batteries: C₆H₅MgCl/AlCl₃/THF (all phenyl complex solutions, APC) and MgTFSI₂/MgCl₂/DME (Mg imide/chloride/DME solutions, ICD). These systems are ideal playgrounds for studying the nature of complex magnesium insertion processes into inorganic hosts. The analysis reported herein shows how the electroanalytical behavior of CP electrodes is affected by the electrolyte solution identity. For instance, the main Mg ions insertion process from the APC solutions occurs at 160 mV lower than from the ICD ones; the heterogeneous rate constant for charge transfer across the interface are significantly higher in APC solutions; in turn, the conversion processes related to the Cu residue in the CP electrodes are kinetically and thermodynamically favorable in the ICD solutions. As expected, the magnesium solid-state diffusion coefficient was found to be solutions independent. The study demonstrates the sensitivity of electroanalytical tools such as slow scanning rate voltammetry for reflecting fine structural changes during intercalation processes and can be generalized to other systems.

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1. Introduction

Electrochemical energy storage and conversion, namely, batteries are critically important for advancing sustainable humanity future. In many domains it is vital, as well as the Achilles hill, in the development and use of mobile electronics, wireless power tools, grid management and mobility. Nowadays, Lithium-ion batteries, usually composed of intercalation anode and cathode materials, are the most advanced commercially used battery technology. However, battery systems contain metallic anode are expected to deliver higher energy density. This is due to three factors: metallic anode materials possess lower reduction potential than any analog intercalation compound, metallic anodes carries much higher specific capacity compared to intercalation materials and metallic anodes might not need components such current collectors or binders [1,2].

Among all elements, magnesium is one of the most promising

candidates as anode material for beyond Li-ion batteries systems. It shows high volumetric and gravimetric capacity, low reduction potential and low price. In addition, Mg possess several advantages over lithium, especially in terms of high abundance, safety, and environmental issues [1,3–6].

However, the development of rechargeable magnesium batteries has been hampered by several challenges explained in details elsewhere [1,2,7].

One important feature of Mg batteries is that the electrochemical activity of Mg anodes and intercalation cathodes is strongly dependent on the nature of the electrolyte solutions even when small variation are involved [2,8]. Magnesium electrolyte solutions chemistry is also considerably more complicated than any analogous lithium system. Most viable known magnesium electrolyte solutions contain complex ions in dynamic equilibrium rather “naked” or simply solvated ions. Among the viable electrolyte solutions, APC and MgTFSI₂+MgCl₂/DME solutions are considered very important because they allow reversible magnesium deposition alongside intercalation of Mg ions with some cathode materials. These two systems belong to two important

^{*} Corresponding author.

E-mail address: raniattias@gmail.com (R. Attias).

families of electrolyte solutions: organometallics-based and “simple salts” ones. These two electrolyte solutions contain different electroactive species, $[5\text{DME}\cdot\text{Mg}_3\text{Cl}_4]^{2+}$ and $[6\text{THF}\cdot\text{Mg}_2\text{Cl}_3]^+$ for $\text{MgTFSI}_2+\text{MgCl}_2/\text{DME}$ and APC solutions respectively [9,10]. It had been shown that both magnesium deposition/dissolution and intercalation/deintercalation proceed through different mechanisms in the two solutions. The processes dynamics are different, and they show different thermodynamic and kinetic attributes. We believe that the different electrochemical responses stem from several factors, all related to solution structures. To understand the relationship between the solution structure and the electrochemical processes one has to take into account interfacial, thermodynamic and kinetic aspects of the reaction's pathways. For instance, de-solvation, stripping of ligands and ligands exchange are expected to have direct and strong influence on the interfacial reactions. The presence of any form of surface, interphase species should certainly have a very strong influence on electrochemical reactions. In the case of intercalation electrodes, additional factors have to be studied, like phase transitions, solid-state diffusion and other aspects pertaining to the reaction's pathways taking place within the materials.

In the current research we studied the effect of the electrolyte solution identity on the electrochemical behavior of Mo_6S_8 cathodes during Mg ions intercalation. Several aspects of the electroanalytical response have been studied, particularly rate determining step of the voltammetric behavior, rate of charge transfer across the interface, and the solid-state diffusion kinetics. This study clearly shows that the electrolyte solution in rechargeable magnesium systems has very strong impact on the cathode's electrochemical behavior. The nature of the solution plays decisive role on the full-cell voltage (and, thus, on the specific energy density) and the interfacial electrochemical response.

2. Methods

2.1. Materials

MgTFSI_2 (99.95%), was purchased from Solvionic. Anhydrous MgCl_2 (99.95%) and AlCl_3 (99.999%) were purchased from Sigma-Aldrich (enclosed in glass ampoules). Phenyl magnesium chloride (2 M solution in THF), Dimethoxyethane (DME), and tetrahydrofuran (THF) were also purchased from Sigma-Aldrich. MgTFSI_2 was dried under dynamic vacuum for 24 h at 250 °C. The solvents were dried with 4 Å activated molecular sieves. The water content in the DME and THF was examined via Karl-Fischer titration (652 KF coulometer, Metrohm) and was kept below 20 ppm. $\text{Cu}_{0.09}\text{Mo}_6\text{S}_8$ (Cu content was determined by ICP) was obtained from NEI Corp. USA. The surface area of the $\text{Cu}_{0.09}\text{Mo}_6\text{S}_8$ was measured using Brunauer-Emmett-Teller technique (Quantachrome, Boynton Beach, FL, U.S.A.) and found to be 7.73 m^2/gr .

All sample preparations and electrochemical measurements were carried out in under high-quality Ar-filled glovebox (MBraun), with water and oxygen levels below 1 ppm.

2.2. Electrolyte solutions synthesis

“All phenyl complex” (APC) electrolyte solution was synthesized by adding slowly and carefully AlCl_3 into PhMgCl/THF solution to the desired concentrations. The final electrolyte solution was composed 0.25 M AlCl_3 and 0.5 M PhMgCl in THF. The resulting solution was stirred during 24 h at room temperature. Quality analysis for the solution was based on the well-known features of the reversible magnesium deposition by CV.

The 0.25 M $\text{MgTFSI}_2+0.5$ M MgCl_2/DME (ICD) electrolyte solution was prepared by adding MgCl_2 into $\text{MgTFSI}_2/\text{DME}$ solution. The

resulting solution was stirred for 24 h at room temperature.

2.3. Electrochemical characterization

$\text{Cu}_{0.09}\text{Mo}_6\text{S}_8$ (denoted from here as CP) composite electrodes were made by spin-coating 1 cm^2 platinum foil current collectors with a slurry of the active material (80 wt %), carbon black (10 wt %), and polyvinylidene difluoride (PVDF, 10 wt %) diluted with isopropanol (2-propanol or isopropyl alcohol) Mass load of ca. 1 mg/cm^2 dry matter.

The electrochemical experiments were carried out using multi-channels potentiostat/galvanostat (VMP-3, Bio-Logic Co.). All electrochemical measurements were conducted in three electrodes flooded cells, composed of CP as working electrode (WE) and magnesium foil as counter (CE) and reference electrodes (RE) (wide and very narrow, respectively). The Mg foils were mechanically cleaned in the glovebox by scraping them with a glass blade in order to remove the native oxide layer before use. All CV curves and all the electroanalytical measurements were carried out after 6–8 preliminary CV cycles, during which the systems attained steady-state equilibrium.

3. Results and discussion

3.1. Qualitative analysis of the slow sweep rate cyclic voltammetry

The aim of the work described in this section was to determine qualitatively, how the electrolyte solutions' nature (the electroactive complexes and the solvents) influences the kinetics and the thermodynamics of the intercalation process into the CP electrodes selected for this study. It is important to note that the fact that the Chevrel phase material used herein include a few percent of copper is very important. It provides an extra red-ox activity which enable to emphasize clearly solutions effects, as described later herein.

For this study, high resolution slow scan rates CV (SSCV) was proven as a very useful electroanalytical tool. Fig. 1 presents SSCV responses of the CP electrodes in APC and ICD at three different scan rates.

The voltammograms in Fig. 1 reflect several cathodic and anodic processes. The basic electrochemical responses of $\text{Cu}_x\text{Mo}_6\text{S}_8$ electrodes and the structural changes they reflect are well known [11]. In brief, the structure of these materials includes octahedral clusters of Mo_6 confined in cubes of S_8 . Between each 2 Mo_6S_8 cell unites there are 2 sets of 6 intercalation sites each (denotes as inner and outer rings of sites) that can accommodate 2 Mg ions (one per ring of sites). The initial response of these materials includes indeed insertion of two Mg ions per unit cell to form $\text{Mg}_2\text{Mo}_6\text{S}_8$. The first insertion process of Mg ions into the outer sites is lousy (Fig. 1 peak a). This is well reflected by the broad corresponding anodic peak b in the range 1.4–1.6 V. At room temperature a fraction of Mg ions remains trapped in the outer rings of intercalation sites and thereby at steady state the first reversible process (peak a) involves only partial insertion of Mg ions. In turn, the second process (Fig. 1 peak c) involves a fully reversible insertion of one Mg ion per unit cell, accommodated by the inner intercalation sites. Anodic peak d reflects the fast de-intercalation of the second Mg ion. When the CP includes any fraction of residual Cu, Mg ions insertion involves a very complex reversible extrusion of atomic clusters of Cu reflected herein in the small cathodic peaks e, f to which the small anodic peaks g, h, i belong. Hence, very the minor amount of Cu detected by ICP is clearly reflected by the voltammetric response of this material. Due to the small amounts of Cu in the CP studied herein, features e – i in charts 1a,b are rather small. We work intentionally herein with this material in order to emphasize the sensitivity of the electro-analysis that was applied. The CVs measured with the

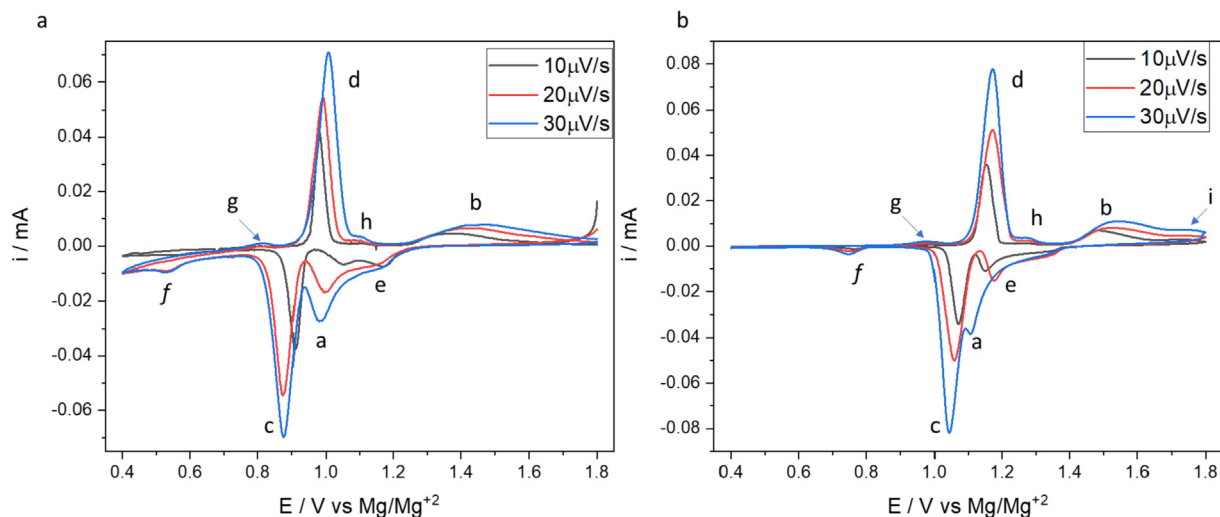


Fig. 1. Steady-state slow scan rate cyclic voltammograms for $\text{Cu}_{0.09}\text{Mo}_6\text{S}_8$ electrodes in (a) $\text{MgTFSI}_2+\text{MgCl}_2/\text{DME}$ (ICD) and (b) APC electrolyte solutions.

two solutions yielded basically similar electrochemical responses, but with a significant potential shift. The cathodic peaks in the voltammograms related to APC solutions appears at potentials 160 mV higher compared to those measured with ICD solutions: The formal potential of process c is around 1.11 and 0.945 V vs Mg in APC and ICD solutions respectively. These potential differences were consistent throughout all the study. This observation for the development of practical rechargeable magnesium batteries, since their energy density is linearly proportional to the cells' potentials. Based on extensive experience with Mg non-aqueous electrochemistry we know that an important factor which determines the over-potential developed at any electrode/solution interface in reactive Mg based electrolyte solutions relates to solvation/desolvation interactions of Mg ions. The situation with ethereal Mg salt solutions are complicated than most of other solutions containing metallic based electrolytes (e.g. Li, Na, K, Fe). There are, apparently, several mechanisms that lead to this complexity: in many cases (especially ethereal solutions) magnesium electrolyte solutions contain complex-cations, frequently in equilibrium with other solution species. This in contrast to simple solvated ions or/and ion-pairs as in most of monovalent ions solutions. Surface phenomena at the metallic Mg RE-solution interface also play an important, not fully predictable role. It is important to note that there were consistent differences in the coulombic efficiencies associated with cycling CP electrodes in the two solutions. While in APC the coulombic efficiency was very close to 100%, in ICD solutions it reached around 85–90%. In light of previous studies of CP electrodes [11–16] the lower faradaic efficiency obtained in ICD solutions does not reflect mismatch in charges related to the intercalation/deintercalation processes. It rather reflects irreversible parasitic reactions associated with TFSI, as had been reported before [8,17–19]. It had been reported that TFSI, despite being envisaged as very stable species, does irreversibly reacts electrochemically even under mild conditions. Thereby, we believe that the intrinsic coulombic efficiency associated with the insertion and de-insertion of Mg (and Cu) with CP electrodes in $\text{MgTFSI}_2+\text{MgCl}_2/\text{DME}$ is very high.

The shape of the CVs which reflect the electrochemical response related to Mg intercalation/de-intercalation (features a – d) and Mg $\langle\text{---}\rangle$ Cu displacements (features e – i) is strongly affected by the solutions' nature. The peaks' separation in the CVs related to the ICD solutions is sharper (e.g. a better separation among the cathodic peaks a, c and e). This indicates that the slower (first) Mg

intercalation process and the first Mg–Cu displacement stage are more thermodynamically favorable in ICD than in APC solutions. Furthermore, the electrochemical activity of these processes seems to be is higher in ICD vs. APC solutions, as reflected at the higher scan rates ($>20 \mu\text{V/s}$). Interestingly, at scan rate of $30 \mu\text{V/s}$ the voltammetry of these cathodes in APC solutions resembles that for pure, Cu-free Mo_6S_8 electrodes except for the small reduction peak f and oxidation peak h which remain indicative of the $\text{Cu}_x\text{Mo}_6\text{S}_8$ phase [20]. These results suggest that the electrochemical activity of these CP electrodes related to the Mg–Cu displacement, is kinetically slower in APC than in ICD solutions.

All these results point towards significant influence of the solution nature on the thermodynamic and kinetic properties of both electrochemical processes (i.e. Mg ions intercalation into $\text{Cu}_x\text{Mo}_6\text{S}_8$ and Mg–Cu displacements from the host). It is important to note, that the well-defined and separated peaks related to these two individual processes enable the analysis of each process separately. Combined with previous studies, showing that the electrochemical activity of CP electrodes is electrolyte solution and electrodes' composition dependent in a well resolved manner [13,20], leads to the inference that these findings also hold for electrodes comprising Cu free CP.

Additional interesting feature is seen in Fig. 1. The two main redox peaks potentials are scan-rate dependent in the two solutions, although to different extent. At such low scanning rates it cannot be related to the effect of an IR drop (with an influence of the specific solutions' conductivity on it). In both cases reduction peaks a and c shift to lower potentials as the potential scanning rate increases from 10 to $30 \mu\text{V/s}$. In ICD solutions a shift of 39 mV in peak c is seen by increasing the scanning rate from 10 to $30 \mu\text{V/s}$, whereas in APC solutions the shift is 11 mV, more than 3 times lower. Such response indicates that the intercalation process associated with the most pronounced Mg intercalation process (reflected by peak c) reaches equilibrium faster in APC than in ICD solutions.

3.2. Rate determining steps of the voltammetric response: semi-infinite diffusion versus ion accumulation in the solid host

Cyclic voltammetry at wide potential scanning rates is a very powerful analytical technique. In fact, for many electrochemically active materials, CV may be much more sensitive and accurate than spectroscopy, microscopy and XRD for detecting structural and

chemical changes [21]. Quantitative and qualitative information can be deduced by comprehensive interpretation of voltammograms, especially when using appropriate mathematical models [22].

Electrochemical intercalation reactions are distinguished from classical electrochemical reactions involving redox couples in solution phase or at interfaces. In classical electrochemical reactions two limiting factors may be usually encountered: charge transfer across the interface and electroactive species diffusion in the solution. With intercalation reactions there can be at least three limiting factors and they involve at least two interfacial charge transfer processes: solution/active mass and active mass/current collector. They also involve bulk redox reactions and solid state diffusion within the host material. Under many circumstances, the significance of these processes as rate determining steps may change with increasing potential scanning-rate in the following order: charge transfer across the interface, infinite solid-state diffusion, semi-infinite solid-state diffusion, and accumulation of intercalated species within the host bulk [23]. These limiting factors, or rate determining steps (RDS), can be identified and quantified using cyclic voltammetry at different scan rates.

In the case of solid-state diffusion limited behavior with semi-infinite boundary conditions the peak current (I_p) vs. scan rate (ν) function may be expressed by the Randles-Sevcik equation:

$$I_p = 2.69 \cdot 10^5 n^{1.5} A \sqrt{D \nu} \Delta C$$

where n is the number of the electrons involve in the specific reaction, A is the electrode real surface area obtained from BET measurements, D is the solid-state diffusion coefficient, and ΔC is the change in the Mg ions concentration inside the host material during the specific stage.

It is important to note that equation 1 was developed for Nernstian redox reactions across single interfaces with a constant electroactive bulk concentration. In addition, this equation is correct only for reversible redox reaction. Also, the theory relates to systems which diffusion coefficient is constant, potential invariant. This may not be the case for solid state diffusion of many intercalation electrodes. However, Randles-Sevcik equation may be adequate as a first approximation for the situation around the peak's potential, because a very small amount of charge is injected around the peak potential, compared with the entire process [23].

In contrast to semi-infinite diffusion limited process, accumulation limited process can be characterized by the following relationship, which related to Langmuir type isotherm:

$$I_p = 9.39 \cdot 10^5 \nu l A \Delta C$$

where l is the electrode thickness.

The analysis described below relates to the two consecutive Mg ions insertion processes denote in Fig. 1 as peaks a and c.

Fig. 2 shows the peak current as a function of the scanning rate for the 2 magnesium intercalation processes in the two solutions (i.e. APC and MgTFSI₂+MgCl₂/DME)

Analyzing the peak current vs. scanning rate curves for ICD solutions reveal interesting voltammetric behavior. The first intercalation process indexed as peak a exhibits two scanning rate dependences limiting behaviors. At slow scan rates (10–50 μ V/s) the peak current is linearly proportional to ν . Hence, at the slow scan rates the intercalation process associated with peak a is accumulation controlled. At higher scan rates the peak current fits better to $\sqrt{\nu}$, indicating that the process is under solid state diffusion control.

On the other hand, the second Mg intercalation process, associated with peak c, shows that the peak current fits well linear

correlation with $\sqrt{\nu}$ rather than ν , even at the slowest scan rates (included (0,0) point). This indicates that the magnesium insertion reaction related to peak c (actually the main Mg intercalation process), is mainly controlled by semi-infinite solid-state diffusion. Interestingly, even at the slowest scan rate in this study, 10 μ V/s, this current/voltage response of this process does not conform to accumulation-controlled reaction (does not reach quasi-equilibrium).

Another interesting insight can be learned from peak f, which is associated directly to concomitant Mg intercalation and copper extrusion (i.e. Mg–Cu displacement). Peak f shows no relation to any typical limiting behavior discussed above. This indicates that this conversion step exhibits different limiting behavior during CV, associated with different reaction dynamics, rather than simple charge transfer across the interface, solid state diffusion or accumulation. It might constitute mixed kinetics associated with several internal, solid-state, and interfacial processes.

The electrochemical intercalation reactions in APC exhibit also two limiting cases.

The magnesium insertion reaction related to peak a (the first Mg intercalation process) exhibits a single limiting behavior, in contrast to the situation in the ICD solutions. The peak current shows better linear relations to $\sqrt{\nu}$ all over the tested scan rates. However, there are two linear regions in the I_p vs. $\sqrt{\nu}$ curve (10–20 and 30–200 μ V/s). The results indicate that the intercalation process associated with peak a may become accumulation-controlled only at the extreme low scan rates.

The second magnesium intercalation process, peak c, exhibits two limiting behaviors depending on the scan rates. At slow scan rates (10–30 μ V/s), the peak current is linearly proportional to ν . Hence, at slow scan rates the intercalation reaction is accumulation-controlled. At higher scan rates, the peak current is linearly proportional to $\sqrt{\nu}$, indicating that the process is under solid state diffusion control.

It is very important to note that any linear fitting in these cases must obtain curve that goes to 0 at the origin, namely, 0,0 point.

As an intermediate conclusion, the data analysis shows that magnesium intercalation kinetics into Cu-containing Chevrel phase electrodes is solution dependent. It comes that the rate determining step of process c has a quasi-equilibrium character at low scan rates in APC. While, in MgTFSI₂+MgCl₂/DME electrolyte solution, the same process is semi-infinite diffusion limited even at the slowest scan rates.

The process associated with peak a (associated mostly with the first magnesium ions intercalation, first stage, and the beginning of copper ions displacement), yields opposite trend. At slow scan rates the electrochemical process in ICD solutions exhibits quasi-equilibrium characteristics, while in APC solutions it is semi-infinite solid-state diffusion controlled, even at the slowest scan rates. The observed rate determining steps of the voltammetric behaviour for a and c processes in APC and ICD electrolyte solutions are summarized in Table 1.

3.3. Solid state diffusion of Mg ions in the Chevrel phase – choosing the right mathematical model

In order to further shed light on the different reaction dynamics of these systems we ran combined CV and GITT experiments. These techniques may yield comparative, indirect, information regarding the electroactive species undergoing insertion into the solid host (i.e. “naked” Mg ions or complex ions). Such data will be used to study the nature of the electrolyte solution influence, if there is any, on the solid-state diffusion of the electroactive ions inside the host material. The calculations of the diffusion coefficients from the CV

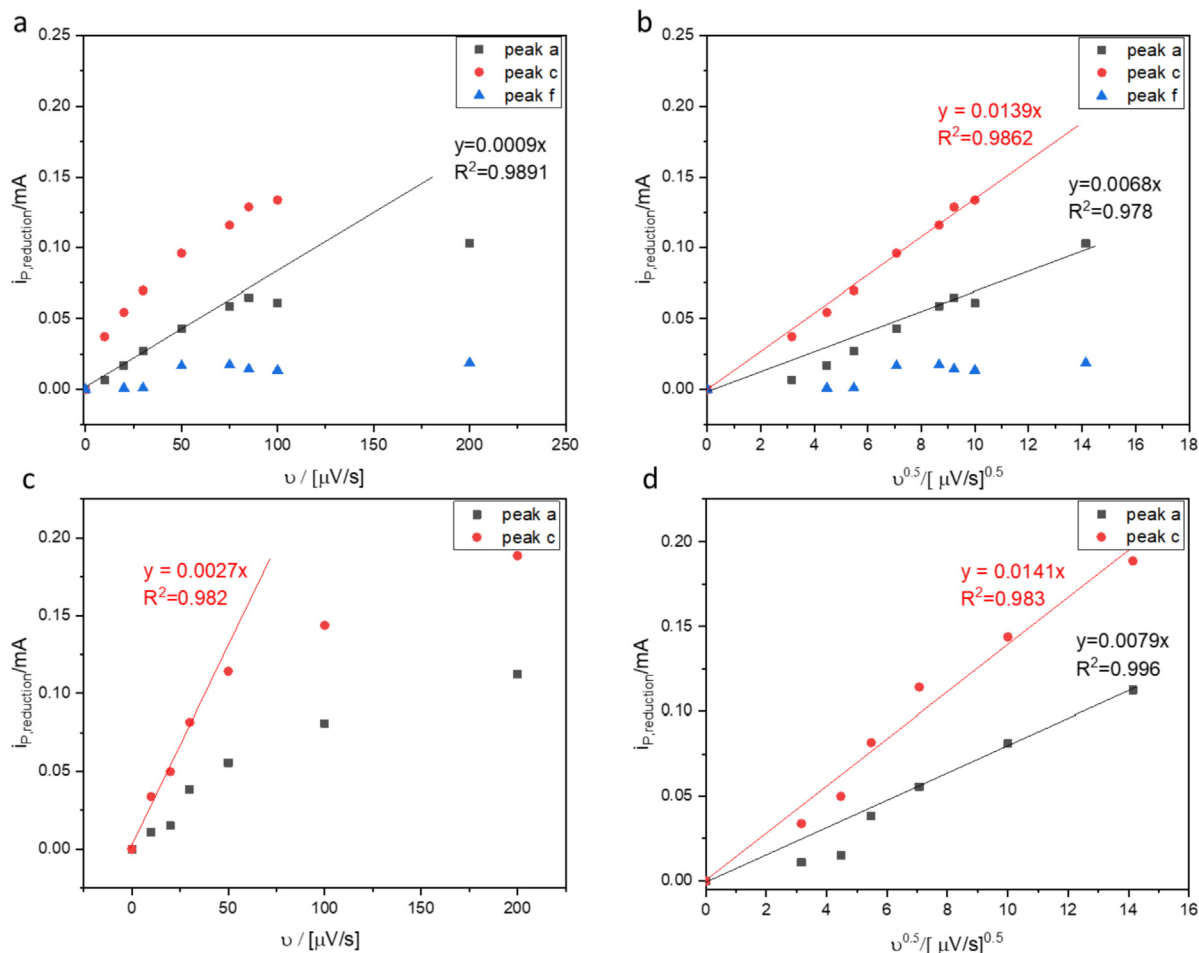


Fig. 2. The dependence of the reduction peaks heights on the potential scan rates for a and c process in (a,b) MgTFSI₂+MgCl₂/DME and (c,d) APC electrolyte solutions.

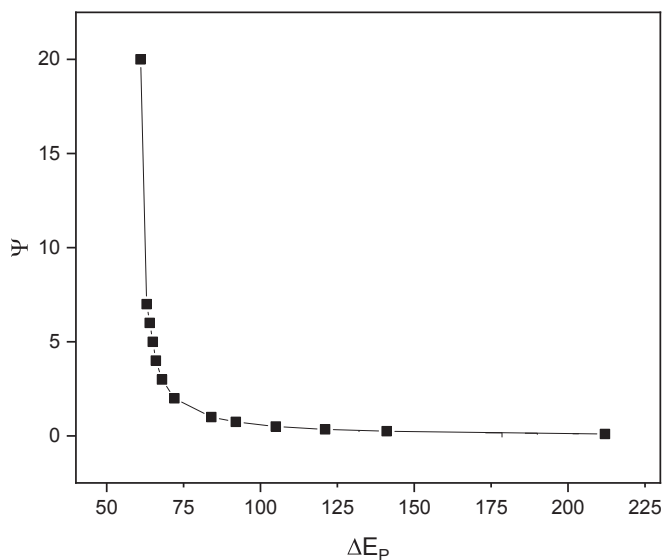


Fig. 3. Dependence of the dimensionless rate parameter from the voltammetric behavior (Ψ) on the peak potential separation (ΔE_p). The data was taken from the experimental values in Ref. [24].

measurements were done using two different models: Nernstian reversible and irreversible reactions. As mentioned above, these

two models were developed for redox process occurring on a single interface while the bulk redox concentrations remain constant. Hence, the quantitative analysis using these models can be considered here only as a first approximation. The calculated diffusion coefficients were compared with the diffusion coefficient calculated from GITT. GITT is especially adequate for the study of solid-state electrochemical processes, as it was developed by solving two differential equations for the second Fick's law with specific boundary conditions of the transient currents. Systematic GITT measurements allow to develop the diffusion coefficient as a function of potential and the content of Mg ions in the host along the intercalation process.

For the reversible Nernstian model equation 1 was used.

For the irreversible redox system, the diffusion coefficients were calculated using the following equation:

$$i_p = 2.99 \times 10^5 \alpha^{0.5} A \Delta c D^{0.5} \nu^{0.5}$$

were α is the transfer coefficient (choose to be 0.5).

The difference in the $i_p(\nu)$ functions for these two models is due to the different boundary conditions used to solve the Nernst-Fick, time-dependent equations. Hence, $i(t)$ and $i_p(\nu)$ functions are different.

For calculating the diffusion coefficients from the GITT response the following equation was used:

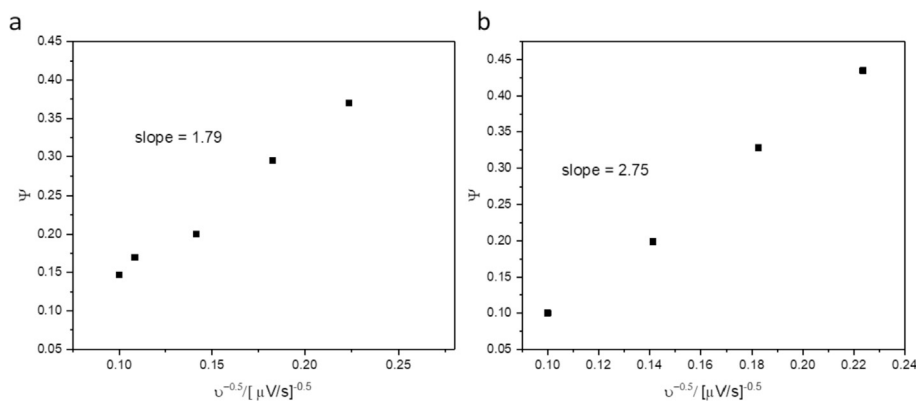


Fig. 4. Dependence of the dimensionless rate parameter of the voltammetry behavior (Ψ) on the scan rate ($\frac{v}{v_0}$). The calculations belong to the processes related to peaks c (Fig. 1), namely, the most pronounced Mg ions intercalation (the second stage). Chart a, b relates to ICD and APC solutions, respectively.

$$D = \frac{4}{\pi\tau} \left(\frac{m_b V_M}{Mw_b S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

where τ represent the duration of the applied current stage, m_b is the electrode active mass, V_M is the molar volume of the electrode material, Mw_b is the electrode's active material molar mass, S is the electrode's surface area (calculated from BET measurements), ΔE_s is the voltage change during the OCV period, and ΔE_t is the voltage change during the galvanostatic polarization stage.

The tabulated results are presented in Table 2.

The data indicate that the solid-state diffusion coefficients are independent on the electrolyte solution identity. This conclusion, while not unexpected, has important implications. The Mg species existing in the two solutions are very different, as well as their solvation shells. For instance, DME is well known to yield very stable Mg-3DME⁺⁺ solvates. These can be expected to intercalate as whole entities. Such co-intercalation eliminates the energy penalty upon disintegration of the solvated ions on the way to release naked Mg⁺² ions and screen the high charge density of the naked ions within the host's crystal. The results point out that even with different electroactive species in the solutions ([5DME•Mg₃Cl₄]²⁺ and [6THF•Mg₂Cl₃]⁺ for MgTFSI₂+MgCl₂/DME and for APC solutions respectively) the ions moving inside the host material diffuse at solutions independent rates. This indicates that the same (probably naked Mg ions) are inserted to the Cu_{0.09}Mo₆S₈. It is expected that very different ionic species will show considerably different diffusion coefficients. It is important to note that the exact value of the diffusion coefficient is meaningless in such calculation, but the order of magnitude is important. The calculations anyway provide approximated average values. Nevertheless, the comparative studies are valuable, since the question is well defined: solution involvement/influence. Also, the measurements and related analyses were carried out in a quite similar manner.

In addition, the above electroanalytical studies used GITT and the calculations of D derived from them as an important indicator, how to use in parallel the CV measurements for calculating the diffusion coefficient. The CV data can be used through calculations

based on the Nernstian reversible reactions model or the model suitable for irreversible reactions. It became clear that for the present study, using a relatively simple model, the former one, was relevant for calculating D from the CV data.

3.4. The effect of the electrolyte solutions on the interfacial charge transfer across the electrodes interface

It has been demonstrated above that Cu_{0.09}Mo₆S₈ electrodes exhibit the same bulk-associated electrochemical characteristics in the different solutions (i.e., the same limiting voltammetric behavior and the same diffusion coefficients). Yet, there are marked differences in the CV responses that raise the assumption that there are still differences in the electrochemical reactions in the two solutions. Moreover, it had been shown in numerous studies that the electrochemistry of magnesium is particularly sensitive to solutions structure. We hypothesize, thus, that the different electroactive species in the solutions have substantial impact on the charge transfer processes across the electrode/solution interface. This dissimilarity should originate from the different activation energies required to strip Mg ions from the different complexes, [5DME•Mg₃Cl₄]²⁺ and [6THF•Mg₂Cl₃]⁺ for MgTFSI₂+MgCl₂/DME and APC respectively. Another possible impact may be related to a difference in the surface chemistry of the CP cathodes in contact with the different electrolyte solutions. For instance, the processes associated with peaks a and f involve the extrusion of neutral Cu atoms to the host's surface, as was explained above. In such instance, strong interactions of Cu with the solutions may lead to differences in the interfacial reactions. In order to test our hypothesis, we calculated the heterogeneous rate constants for Mg ion charge transfer across the electrodes interfaces in both electrolyte solutions.

For that we used the model for quasi-reversible redox systems. Under this framework, the dimensionless rate parameter Ψ must be determined. The heterogeneous rate constant can be determined from the definition of this dimensionless rate parameter, as depicted in the following equation.

Table 1

Summary of the processes limiting factors obtained from I_p vs. v in slow-scan rates with Cu_{0.09}Mo₆S₈ in APC and ICD solutions.

Peak (process)	Slow scan rates		Fast scan rate	
	a	c	a	c
APC	Diffusion controlled	Accumulation controlled	Diffusion controlled	Diffusion controlled
MgTFSI ₂ +MgCl ₂ /DME	Accumulation controlled	Diffusion controlled	Diffusion controlled	Diffusion controlled

Table 2Solid state diffusion coefficients in cm²/s of Mg ions in Mo₆S₈ calculated from CV and GITT measurements.

	peak	Nernstian reversible	Irreversible	GITT
MgTFSI ₂ +MgCl ₂ /DME	a	6 × 10 ⁻¹⁶	8 × 10 ⁻¹⁵	2 × 10 ⁻¹⁶
	c	2 × 10 ⁻¹⁵	2 × 10 ⁻¹⁴	3 × 10 ⁻¹⁵
APC	a	8 × 10 ⁻¹⁶	1 × 10 ⁻¹⁴	8 × 10 ⁻¹⁶
	c	2 × 10 ⁻¹⁵	2 × 10 ⁻¹⁴	1 × 10 ⁻¹⁵

$$\Psi = \frac{\left(\frac{D_0}{D_R}\right)^{\alpha/2} K_S}{\left[D_R \pi \nu \left(\frac{nF}{RT}\right)\right]^{0.5}}$$

where D_0 and D_R are the diffusion coefficients for the deintercalation and intercalation processes. D_0 and D_R were assumed to be equal and were taken from the GITT measurements ($D = 10^{-15}$ cm²/s). F is faraday constant, R is the universal gas constant, T is the temperature, and K_S is the heterogeneous rate constant.

In order to find the linear function $\Psi(\frac{1}{\nu})$ we used the experimental value produced by A.J Bard and L.R Faulkner for obtaining the $\Psi(\Delta E_p)$ function (see Fig. 3) and convert it to $\Psi(\frac{1}{\nu})$ (Fig. 4)[24].

Eventually, the K_S parameters were calculated from the slope of the Ψ vs. $(\frac{1}{\nu})$ curves.

It is important to note that the heterogeneous rate constants for the charge transfer processes across the electrodes interfaces were calculated only for peak c, since the other peaks appears too broad in the CVs we obtained and does not allow to determine the exact peak potential (necessary for the calculations) precisely.

According to this model the heterogeneous rate constant for the charge transfer across the electrodes/solutions interfaces were found as 9×10^{-10} and 1.4×10^{-9} cm/s for ICD and APC solutions respectively. This finding reveals that the charge transfer processes across the electrode's interfaces are faster in APC than in ICD solutions. This is well understood in light of higher interactions of Mg ions with DME compared to THF solutions (concluded from a previous work) [9]. This suggests that the electroactive species in rechargeable magnesium systems may have an important impact on the electrochemical characteristics of the cells by influencing the interfacial electrochemical processes. The diffusion coefficient though, as long as naked Mg ions are inserted into the cathode hosts, remains solutions invariant.

4. Conclusions

The research described herein deals with important questions about the electroanalytical and solid-state electrochemical response of magnesium ions interacting with copper containing Chevrel phase cathodes. We studied, qualitatively and quantitatively, the influence of the electrolyte solutions identity and structure on critical features of CP cathodes' electrochemical processes. These include thermodynamic properties, RDS, diffusion coefficients, heterogeneous rate constant for charge transfer across the electrodes interfaces and some other general features. For this purpose, we compared the electrochemical response of Cu_{0.09}Mo₆S₈ in two important electrolytes solutions, PhMgCl/AlCl₃/THF and MgTFSI₂/MgCl₂/DME solutions.

We have shown that some general features, such the formal potential for the intercalation/deintercalation processes are strongly affected by the electrolyte solutions identity. The intercalation process of Mg ions into Cu_{0.09}Mo₆S₈ electrodes occurs at

higher potential in APC than in ICD solutions. This shows that for practical applications the choice of electrolyte solution may have a great impact on the cells' energy density, even upon using identical electrodes. In addition, the electroactivity related to the Cu residues in the host is also affected by the electrolyte solutions identity. These electrochemical processes, associated with Mg–Cu displacement, are thermodynamically favorable and kinetically faster in ICD than in APC solutions.

We also found that the rate determining steps related to different electrochemical stages during Mg intercalation are affected by the electrolyte solutions. The most important Mg ions intercalation step into Mg_xMo₆S₈ (related to peak c in the CVs, Fig. 1) exhibits a quasi-equilibrium behavior at low scan rates in APC solutions.

The same stage in ICD solutions though, has a semi-infinite diffusion limited process character even at the slowest scan rates. On the other hand, process a, associated with electrochemical reaction of Mg–Cu assemblies, exhibits quasi-equilibrium step in ICD solutions, while in APC solutions the process is semi-infinite solid-state diffusion controlled.

The average solid-state diffusion coefficient of Mg ions into Cu_{0.09}Mo₆S₈ cathodes (during the main process, associated with pick c) was found to be solutions invariant, what means that Mg ions are diffused in the CP host in their naked, un-solvated state. The best equations that can be applied in order to calculate the solid-state diffusion coefficient from the CV response were found to be according to the Nernstian-reversible model.

Interestingly, though not unexpectedly, the electrolyte solution identity influences the interfacial charge transfer processes across the solution/host interface. We found that Mg ions charge transfer kinetics across the solution/electrode interface is faster in APC than in ICD solutions.

This work clearly shows that the nature of the electrolyte solution has a great impact not only on the Mg anode side but also on the electrochemical behavior of the best Mg ions intercalation cathodes (Chevrel phase). This work extends the theoretical basis for developing rechargeable Mg batteries.

CRedit authorship contribution statement

Ran Attias: Conceptualization, Writing - original draft, Investigation. **Shaul Bublil:** Investigation. **Michael Salama:** Investigation. **Yosef Goffer:** Conceptualization, Writing - review & editing. **Doron Aurbach:** Conceptualization, Writing - review & editing.

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