

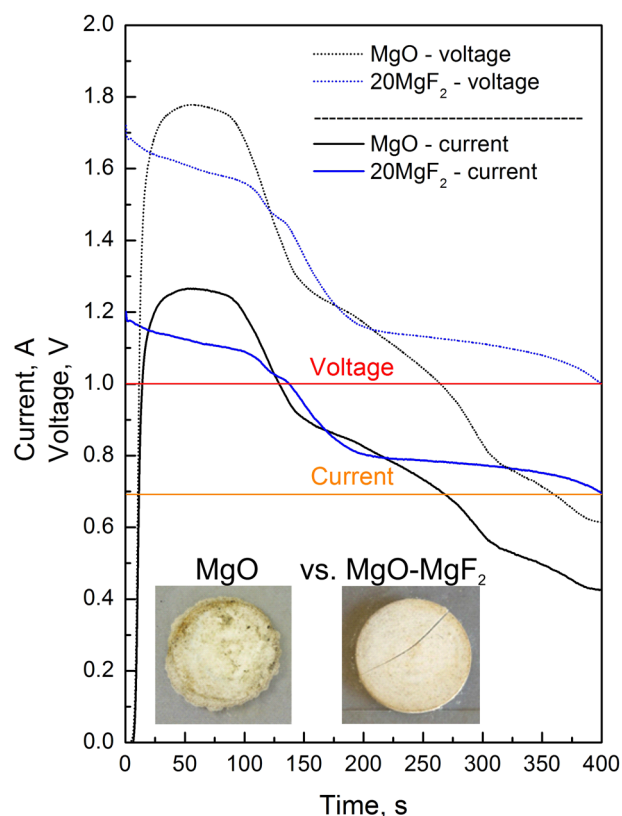
MgO-MgF₂ system obtained by sol-gel method as an immobilizing agent of the electrolyte applied in the high temperature cells

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Abstract A MgF₂-MgO system was tested as an immobilizing agent for the electrolyte KCl-LiCl-RbCl in high temperature cells. Samples of MgF₂-MgO with different contents of MgF₂ (0–20 mol%) were prepared by one-step sol-gel method in the reaction of magnesium methoxide dissolved in methanol with aqueous solution of hydrofluoric acid. The immobilizing agents were characterized by X-ray powder diffraction, low-temperature nitrogen adsorption and thermogravimetric measurements. Dimensional stability, mechanical strength and unfilled spaces were characterized using pellets containing 40 wt% of immobilizing agents. Finally, the pellets were used in an electric cell at 400 °C and the changes in current and voltage were recorded in time. The introduction of MgF₂ to MgO in the synthesis by the sol-gel method significantly improves the textural and mechanical properties of immobilizing agent and ensures longer and more stable work of high temperature cell.

Graphical abstract



Keywords Sol-gel method · MgF₂-MgO immobilizing agent · High-temperature cell · Thermal battery

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1 Introduction

Thermally activated batteries belong to the chemical sources of current employed in special situations, e.g., as reserve power supply systems applied in an emergency. That is why they are used in civilian and military devices. The thermal battery can be exposed to high temperatures, excessive closing force, acceleration force, vibration, shock or combination of all the conditions mentioned above [1]. Its greatest advantage is a 100% reliability even after a long-term storage (minimum 15 years) in extreme environmental conditions (from -50 to $+60$ °C) [2, 3]. The time of battery activation, that is the time between the triggering pulse and the electric energy produced, should be shorter than 1 s. This is the time needed to initiate in the battery case the exothermic chemical reaction that will heat the battery to ~ 400 °C. At this temperature the electrolyte which is a salt (in our batteries a LiCl–KCl–RbCl mixture) gets molten [4]. The molten electrolyte must be kept by the immobilizing agent to prevent its leakage that could lead to short-circuit between cells [1].

The aim of this work was to use for the first time a mixed system MgO–MgF₂ containing 0, 10, and 20 mol% MgF₂, obtained by sol–gel method, as an electrolyte immobilizer. The sol–gel method permits obtaining various materials of large surface area, narrow pore size distribution and well-developed mesoporous structure [5, 6]. Moreover, the sol-gel method offers the possibility of obtaining materials of high purity by one-step synthesis of mixed systems at a low temperature and relatively low cost [7]. The electrolyte in the form of the eutectic LiCl–KCl–RbCl mixture with relatively low melting temperature was selected for the study. The influence of calcination temperature and composition of the immobilizing agent on the physicochemical properties and absorption of the electrolyte as well as ionic conductivity of the mixture of electrolyte-immobilizing agent were determined. Magnesium oxide is a typical and often used immobilizing agent besides SiO₂, Y₂O₃, ZrO₂, TiO₂, AlN, BN, Al₂O₃ (or other inert, nonreactive inorganic ceramic powders) [8–12] and MgF₂ is added to improve the immobilizing effect of MgO and its mechanical and electric properties.

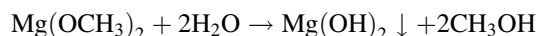
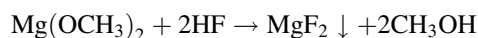
2 Experimental section

2.1 Preparation of materials

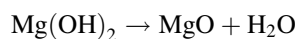
2.1.1 Preparation of MgO–MgF₂ system

A series of MgO–MgF₂ samples of different magnesium fluoride content (0, 10, and 20 mol%) were synthesized by sol–gel method from magnesium methoxide and aqueous

solution of hydrofluoric acid:



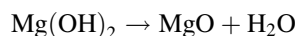
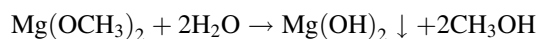
During thermal treatment Mg(OH)₂ is dehydroxylated to magnesium oxide:



The dense gels of Mg(OH)₂–MgF₂ were subjected to ageing for 40 h at room temperature, followed by drying at 80 °C for 3 h. The dry samples were calcined for 4 h at 500 and 600 °C. The MgO–MgF₂ samples were labeled as xMgF₂, where x stands for the mol% of MgF₂ in the sample.

2.1.2 Preparation of MgO

MgO was obtained by the sol-gel method (as MgO–MgF₂ samples) by hydrolysis of magnesium methoxide in water.



The gel of Mg(OH)₂ was treated as the above Mg(OH)₂–MgF₂ system.

2.1.3 Eutectic LiCl–KCl–RbCl mixture

The eutectic LiCl–KCl–RbCl mixture containing 31.54 wt% LiCl, 23.47 wt% KCl and 44.99 wt% RbCl was used as the electrolyte [13]. The concentration of Na⁺ ions, which are the main contaminating component in the electrolyte, was 0.19 wt% and it was determined by inductively coupled plasma atomic emission spectrometer. Specially prepared electrolyte had no traces of H₂O, LiOH, and Li₂O.

The real melting temperature of the electrolyte (302.4 °C) was determined by the differential scanning calorimetry method using a differential thermoanalyzer, model STA 409C 3F, made by Netzsch (Germany).

2.1.4 Preparation of electrolyte pellets

The eutectic mixture consisting of 31.54 wt% LiCl, 23.47 wt% KCl, and 44.99 wt% RbCl was used as the electrolyte. Electrolyte pellets were prepared by accurate mixing (no grinding) of definite amounts of dry electrolyte powders and immobilizing material. The obtained uniform mixtures (1.002 g), containing 40 wt% immobilizing agent, were placed in a pellet machine and pressed at a static pressure of 400 MPa.

2.2 Material characterization

2.2.1 Determination of surface area, pore volume, and pore diameter

Textural characterization of MgO-MgF₂ system calcined at 500 and 600 °C was performed by the low-temperature (−196 °C) nitrogen adsorption-desorption using a sorptometer ASAP 2010 manufactured by Micromeritics (U.S. A.). Prior to the measurements of adsorption-desorption isotherms, the samples were outgassed at 300 °C for 4 h. Surface area was determined by the Brunauer–Emmet–Teller (BET) method, whereas total pore volume and average pore diameter were calculated using Barrett–Joyner–Halenda (BJH) method.

2.2.2 Thermogravimetric analysis

Thermogravimetric analysis of immobilizing agent was performed using fresh (uncalcined) samples in the temperature range of 30–900 °C on a differential thermogravimetric analyzer Setaram TGA equipped with a thermogravimetry (TG) measurement unit. The experiments were performed under air flow (99.995 % purity) at a heating rate of 10 °C min^{−1}. All TG profiles presented in this work were normalized to the same sample weight (100 mg).

2.2.3 X-ray diffraction analysis

The X-ray powder diffraction measurements were performed on a Bruker AXS D8 Advance diffractometer with Ni-filtered CuKα radiation over the 2 θ range of 20–80°.

2.2.4 Measurement of specific volume of the pellet

The experimental specific volume of the pellet was calculated from the quotient of the pellet volume and mass. Pellet volume (25 mm diameter pellet), thickness and weight were determined with the accuracy of 0.0001 cm³, 0.01 mm, and 0.0001 g, respectively [14]. The theoretical pellet volume was determined from the density of the individual pellet components (i.e., KCl, LiCl, RbCl, MgO, MgF₂) and their percentage content in the mixture.

The percentage of void spaces in the pellet was calculated as a difference between the specific experimental volume and the theoretical volume.

2.2.5 Dimensional stability and electrolyte leakage test

The pellet was placed centrally between two quartz plates of 120 mm diameter and transferred to the measuring equipment. The measuring system consisted of heating plates having temperature of 400 °C. The pressure of 60 kPa

was applied to the pellet. A ceramic fitting with a sensor was placed in the center of the quartz plate for monitoring the changes in the pellet thickness (reading accuracy: 0.0001 mm). Thickness changes were recorded for 3 min and then the pellet was taken out and examined visually. It allowed to eliminate samples with low mechanical strength.

2.2.6 Measurement of mechanical strength of the pellet

Mechanical strength of pellets with the electrolyte was measured using a digital dynamometer FT-50 made by Sauter (Germany). The pellet of 25 mm in diameter was mounted in a special holder with two supports of 15 mm in length placed at a mutual distance of 18 mm. The strength needed to break the pellet was measured at half of the distance between the supports. The break was caused by pressing a blade of 15 mm in length. All pellets (immobilizing agent with the electrolyte) used in this work had the same mass (1.002 g) and thickness (1.01 mm). The real volume of pellets was 0.496 cm³.

2.2.7 Electrical test of the cell

A model cell Li / KCl–LiCl–RbCl + immobilizing agent / FeS₂ was tested at 400 °C and 60 kPa pressure by discharging through a 1.32 Ω resistor. The cell was placed between two heating plates having a temperature of 400 °C lined with a thin layer of mica. Voltage and current values were recorded every 0.02 s.

3 Results and discussion

The derivative thermogravimetric analysis (DTG) curves presented in Fig. 1, recorded for MgO-MgF₂ and MgO

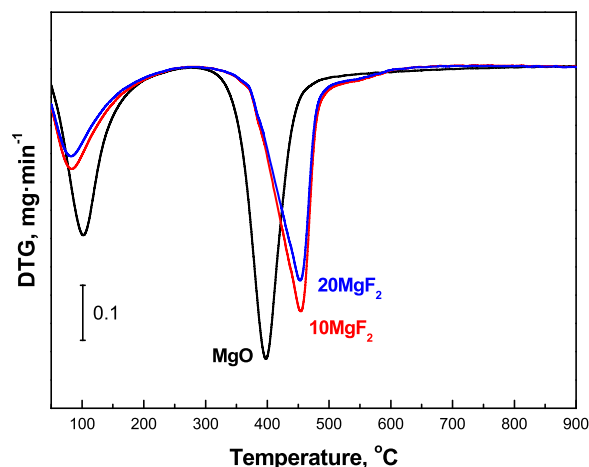


Fig. 1 DTG curves recorded for 10MgF₂ and 20MgF₂ (obtained by sol-gel method) and MgO (used as a reference material)

show two maxima of mass loss. The effects ascribed to physically adsorbed water occurred below 200 °C. The mass loss was proportional to the content of MgO in the sample, which is related to high hygroscopic capacity of this compound. The mass loss related to the decomposition of Mg(OH)₂ to MgO and dehydroxylation of the MgO surface [15] took place at about 390 °C in the case of pure MgO and at about 460 °C in that of the mixed system. Mass loss in the range 320–600 °C, observed for the materials obtained by the sol–gel method from metal alkoxides, is related to dehydroxylation of magnesium hydroxide, although to a certain extent it can also correspond to thermal decomposition of organic residue of the precursor, that is its alkoxy groups [6]. That is why the position of the maximum assigned to the decomposition of –OCH₃ group for sample 10MgF₂ and 20MgF₂ can be shifted towards higher temperatures relative to that for pure MgO. This is a consequence of the presence of fluorine which is a strong nucleophile. The substitution of –OCH₃ group with fluorine

enhances thermal stability of methoxy group, which increases the temperature of its decomposition.

As follows from DTG data, a full decomposition of the precursors of MgF₂ and MgO takes place below 500 °C, so further studies were performed for the samples after the calcination at 500 or 600 °C. X-ray diffraction patterns (Fig. 2) recorded for the samples calcined at 500 °C indicate the formation of a physical mixture of MgF₂ and MgO crystals.

The composition and textural parameters of the immobilizing agent after calcination at 500 and 600 °C were presented in Table 1. The determination of the composition of MgO-MgF₂ samples, performed by the pyrohydrolytic method [16], has shown that in the samples intended to contain 10 and 20 mol% MgF₂ the concentrations of the latter were 12.9 and 20.7 mol%, so they were slightly higher than the planned values. The isotherms of low-temperature N₂ adsorption on MgF₂-MgO and MgO calcined at 500 °C in air are shown in Fig. 3a. They exhibit hysteresis loop of type H2(b) which indicates capillary condensation in mesopores [17]. On the basis of the isotherms recorded for oxofluorides and magnesium oxide, textural parameters were determined. In Fig. 3b the pore size distribution as a function of pore diameters was presented for MgF₂-MgO and MgO samples. The pore sizes, calculated by the BJH method from the isotherm desorption branch, appeared to be strongly dependent on the sample composition and decrease with the introduction of MgF₂ to MgO. All the samples were mesoporous materials with the mean pore diameters varying from 8 to 11 nm after calcination at 500 °C (Table 1 and Fig. 3b). Surface areas of the above systems range from 158 to 351 m² g⁻¹. The results presented in Table 1 indicate that the content of magnesium fluoride has a considerable effect on the surface area and porosity of the MgO-MgF₂ systems. It results from Table 1 that the introduction of 10 mol% MgF₂ increases the surface area by a factor of 2 and the total pore volume by about 50% compared to MgO. For example, surface areas of pure MgF₂ obtained by sol–gel method and calcined at 500 and 600 °C were

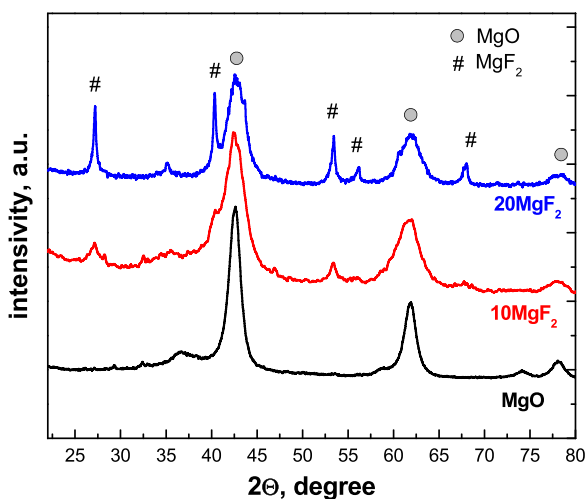


Fig. 2 X-ray diffraction patterns of MgO, 10MgF₂ and 20MgF₂ calcined at 500°C

Table 1 Physical characteristics of MgO and MgO-MgF₂ samples after calcination in air at 500 and 600 °C for 4 h

Sample code	MgF ₂ content, (pyrohydrolysis)* mol%	Temperature of calcination, °C	BET surface area, m ² g ⁻¹	Total pore volume, cm ³ g ⁻¹	Average pore diameter, nm
MgO	0	500	158	0.45	11.3
		600	102	0.43	16.9
10MgF ₂	12.9	500	351	0.72	8.3
		600	293	0.64	8.8
20MgF ₂	20.7	500	301	0.67	8.8
		600	257	0.60	9.3

* The measurement of fluoride content in MgO-MgF₂ samples was based on the use of pyrohydrolysis for sample decomposition (in the flow of air and steam), followed by potentiometric determination (fluoride ISE) of the analyte in total ionic strength adjustment buffer [16]

Fig. 3 Nitrogen adsorption-desorption isotherms **a** and pore size distributions **b** for 10MgF₂ and 20MgF₂ and MgO calcined at 500 °C

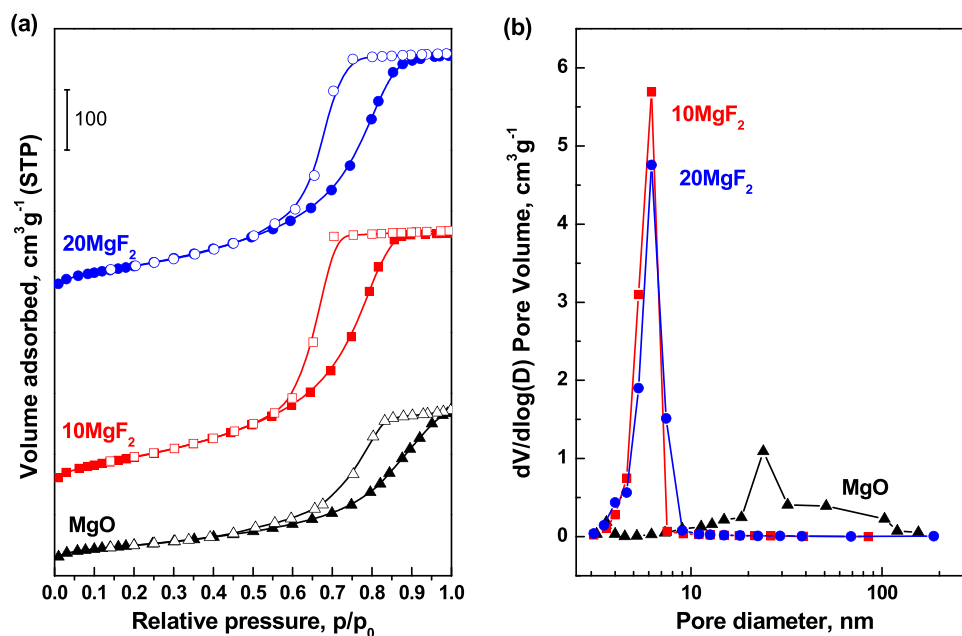


Table 2 Results of the measurements of dimensional stability (%), mechanical strength (*N*) and the unfilled space (*V* %) in the pellets containing MgO, 10MgF₂ or 20MgF₂ as immobilizing agents. Concentration of the immobilizing agent in the pellet was 40 wt%


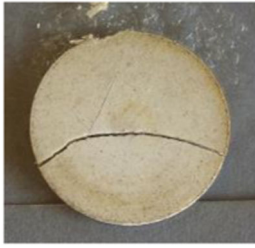

Calcination temperature of the electrolyte immobilizing agent, °C	MgO			10MgF ₂			20MgF ₂		
	%	<i>N</i>	<i>V</i> %	%	<i>N</i>	<i>V</i> %	%	<i>N</i>	<i>V</i> %
500	7.6	4.1	47.8	4.1	4.1	66.7	2.0	6.9	64.8
600	17.6	3.7	43.1	5.6	4.8	59.9	2.9	5.3	57.6

23 and 19 m² g⁻¹, respectively [7]. This is why a simple mechanical mixture of MgO and MgF₂ would not improve these parameters. The BET surface area of MgO was two or three times smaller than that of MgO-MgF₂. The surface area was also influenced by the calcination temperature as indicated by the reduction in surface area of immobilizing agents after the calcination at 600 °C (Table 1). The obtained results permit to conclude that from the textural viewpoint the MgF₂-MgO systems are not simple mechanical mixtures of MgF₂ and MgO, but they are composites with a new porous structure.

The MgO and MgO-MgF₂ samples were tested as electrolyte immobilizing agents. Electrolyte pellets were prepared from dry electrolyte (KCl–LiCl–RbCl) powders and an immobilizing material (MgO or MgO-MgF₂). The pellets made of these materials were characterized by determining absorption capacity of the electrolyte, mechanical strength and volume of voids. The absorption capacity was measured as a change in the thickness of a pellet containing 40 wt% of immobilizing agent mixed with the electrolyte. The dimensional stability defines the percentage of reduction in thickness of the initial pellet at 400 °C under static pressure of 60 kPa.

In the test conditions some amount of the electrolyte is pressed out of the pellet, so the electrolyte leaks out. The pellets showing smaller changes in thickness are characterized by a higher absorption capacity. As evidenced by data given in Table 2, the highest absorption capacity was shown by the 20MgF₂ samples. The 10MgF₂ samples were characterized by twice greater leaks, while the poorest absorption capacity was obtained for MgO alone. The absorption capacity of the electrolyte depends on the calcination temperature of the immobilizing agent; the higher the calcination temperature the lower the capacity. Results of mechanical strength measurements proved the highest value of this parameter for 20MgF₂ and the lowest for MgO, so it changed in the same sequence as the absorption capacity. Higher calcination temperature causes a reduction in the mechanical strength, as observed for MgO and 20MgF₂ samples. At higher calcination temperature (600 °C) of the immobilizing agent its porosity is reduced which results in a decrease in the ability to absorb the electrolyte that remains on the pellet external side thereby causing a greater breakability.

Table 3 Photographs of pellets made of the electrolyte and MgO, 10MgF₂ or 20MgF₂ as immobilizing agents (obtained by sol–gel method and calcined at 500 or 600 °C, followed by the introduction to the electrolyte in the amount of 40 wt%)

Calcination temperature of the electrolyte immobilizing agent, °C	MgO	10MgF ₂	20MgF ₂
500			
600			

The volume of voids (V , %) took similar values for the immobilizing agents with MgF₂ and a value by $\sim 1/4$ lower for MgO sample.

To sum up, from among the immobilizing agents studied the MgO-MgF₂ system containing 20 mol% MgF₂ was found to show the best performance. It shows the strongest immobilizing effect, has the highest mechanical strength and large volume of voids that can be filled with molten electrolyte.

Analysis of the pellets after the pressure tests (Table 3) confirmed that the most pronounced deformations were noted for the pellet with MgO. Particularly great amount of the electrolyte leaks out from the tablets containing MgO calcined at 600 °C. The pellets containing 10MgF₂ and 20MgF₂ show a good stability and practically no leakage of the electrolyte. As the electrolyte leakage leads to short-circuit between the cells and has a deteriorating effect on the battery performance, the best one from the materials tested was MgO-MgF₂ containing 20 mol% MgF₂. No breaking up was observed immediately after measurements but the pellets broke up after cooling to room temperature. The breaking up can be related to inhomogeneous cooling of the pellets after removal from the measuring device, which could generate a thermal stress in the material [18].

At the final stage of the study, the thermal batteries made of cells with MgO and 20MgF₂ as immobilizing agents were tested for their ability of electric power generation at

400 °C. Figure 4 presents time dependences of voltage and current intensity changes. In the first 100 s of work the cell with MgO showed a bit higher values of voltage and current intensities. However, with time passing, these values rapidly decrease and the work of battery with cells filled with 20MgF₂ is more stable. For the latter battery the voltage is stabilized at 1.1 V generating current of 0.8 A.

Based on the above measurements it can be concluded that the MgF₂-MgO immobilizing agent, obtained by sol–gel method, could be potentially used in thermal batteries. Its texture, volume of channels inside the pellet, dimensional stability during the measurements and electrical test of the cell are favorable for this concept.

4 Conclusions

1. The introduction of MgF₂ to MgO in the synthesis by sol-gel method significantly improves the textural and mechanical properties of immobilizing agents towards the LiCl–KCl–RbCl electrolyte.
2. The mixed MgO-MgF₂ materials show much better ability to bind molten electrolyte than MgO alone.
3. The cell with 20MgF₂ as the immobilizing agent ensures a longer and more stable work than that based on MgO.

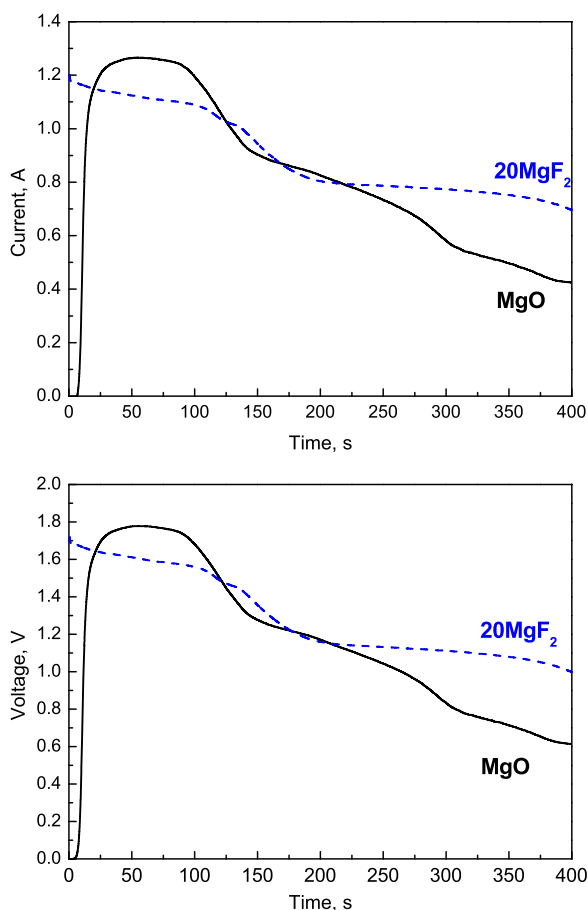


Fig. 4 Electric characteristics of the tested cells as a function of current vs. time and voltage vs. time. Immobilizing agent (40 wt%) calcined at 500°C—solid line: MgO, dashed line: 20MgF₂

- The mixed MgO-MgF₂ systems were shown to be an attractive alternative as immobilizing agents due to their capability of improving the performance of thermal cells.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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