

Article

MgO Modified with MgF₂ as an Electrolyte Immobilizing Agent for the High-Temperature Cells

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Abstract: Magnesium oxide, generally applied as a filler in high-temperature cells (with an electrolyte melting point above 250 °C), was modified with magnesium fluoride to improve its mechanical and electrical properties. Samples containing 10 and 25 mol.% MgF₂ were prepared and calcined at 500, 600, and 700 °C. They were characterized by low-temperature nitrogen adsorption and X-ray diffractometry (XRD). Moreover, the electrolyte absorption, mechanical strength of pellets made of filler and electrolyte, and volume of unfilled spaces were determined. It was shown that the introduction of MgF₂ in the amount of 10 and 25 mol.% results in a considerable decrease in the surface area of the initial MgO, which testifies to the covering of MgO by the formed fluoride. However, no new crystalline phases were formed as concluded from the XRD analysis. The pellets consisting of electrolyte and MgF₂/MgO filler (the electrolyte + 40 wt.% of the filler) had a higher mechanical strength compared to bare MgO filler. In particular, they outperformed MgO in the ionic conductivity of molten electrolyte. The latter was almost three times as high as that of MgO filler, when the filler containing 25 mol.% MgF₂ was employed. The aforementioned properties of MgF₂/MgO materials predispose them for use as fillers in high-temperature cells.

Keywords: MgF₂-MgO; fluorides; oxyfluorides; immobilizing agent; high-temperature cell; thermal battery

1. Introduction

Thermal batteries are counted among the chemical power sources utilized in the supply of power for special devices. They are characterized by a high impact resistance as well as endurance against vibrations and overload. A single cell contains an electrolyte immobilized in a filler, besides an anodic and cathodic material. In the environmental temperature range from −50 to +70 °C, the electrolyte–filler mixture has insulator properties. After heating the cell to temperatures above 300 °C, the electrolyte undergoes melting and becomes an ionic conductor [1]. In a single cell, the electrolyte is mixed with a filler, which is intended to prevent the molten electrolyte from leaking out of the cell without limiting the ionic conductivity of the electrolyte. For this reason, the filler should possibly have a low density, good wettability, and chemical resistance to the action of the molten electrolyte, while maintaining an appropriate mechanical strength [2]. The fillers applied in practice are: SiO₂, MgO, ZrO₂, BN, Y₂O₃, and TiO₂ [3,4].

Magnesium oxide is a commonly used filler for the immobilization of the molten electrolyte (which is a mixture of alkali metal chlorides) at the operation temperature of high-temperature cells. Before activation, the electrolyte is a solid and this is why it does not self-discharge for at least 15 years. It is only after melting caused by a thermal stimulus at above 300 °C that the cell reaches the rated voltage and electric current intensity is no longer than 1 s—this process is called cell activation. Molten

electrolyte leakage and cracks in the filler–electrolyte pellets result in a reduction in the cell efficiency and internal short circuits. The task of the molten electrolyte is to provide good ionic conductivity between the electrodes. Since the filler itself is an insulator at the cell operation temperature, the electrolyte/filler ratio must be limited.

It was found in earlier studies that mixed systems of MgF_2 - MgO prepared by co-precipitation are characterized by better immobilizing properties than bare magnesium oxide [5,6]. In the present study, we subjected MgO to a modification consisting in the generation of a magnesium fluoride layer on the MgO surface. This is a considerably simpler method for the preparation of MgF_2 - MgO systems compared to the co-precipitation [5] and sol-gel [7] methods.

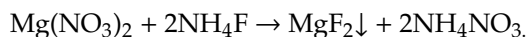
2. Materials and Methods

2.1. Preparation of Materials

2.1.1. Preparation of MgO and MgF_2 - MgO System

The MgO sample was obtained by thermal decomposition of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (POCH–Polish Chemicals Reagents) under air flow at 500°C for 4 h.

A series of MgF_2 - MgO samples of different contents (10 and 25 mol.%) of MgF_2 were synthesized by the impregnation of MgO calcined at 500°C with an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and followed by the addition of an aqueous solution of NH_4F :



The formed MgF_2/MgO was centrifuged and washed with distilled water. Then, it was dried at 120°C for 10 h. The dry samples were calcined for 4 h at 500, 600, and 700°C under air flow. The MgF_2/MgO samples were labelled as xMF, where x stands for mol.% of MgF_2 in the sample.

2.1.2. Eutectic LiCl - KCl - RbCl Mixture

Eutectic LiCl - KCl - RbCl mixture containing 31.54 wt.% LiCl , 23.47 wt.% KCl , and 44.99 wt.% RbCl was employed as the electrolyte [5]. The concentration of Na^+ ions, which are the main contaminating element in the electrolyte, was less than 0.19 wt.% as determined by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES) plasma spectrometer. The specially prepared electrolyte had no traces of H_2O , LiOH , and Li_2O .

The real melting point of the electrolyte was 302.4°C as determined by differential scanning calorimetry on a differential thermoanalyzer, model STA 409C 3F (Netzsch, Selb, Germany).

2.1.3. Preparation of Electrolyte Pellets

The eutectic mixture described above was used as the electrolyte. The electrolyte pellets were prepared by accurate mixing (not grinding) of definite amounts of dry electrolyte powders and the immobilizing material. The obtained uniform mixtures, containing 40 wt.% immobilizing agent, were placed in a pellet-making 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

The textural characterization of MgF_2/MgO systems calcined at 500 and 600°C was obtained by the low-temperature (-196°C) nitrogen adsorption using a sorptometer ASAP 2010 (Micromeritics, Atlanta, GA, USA). Prior to the measurements of the adsorption–desorption isotherms, the samples were outgassed at 300°C for 4 h. The surface area was determined by the Brunauer–Emmett–Teller (BET) method, while the total pore volume and average pore diameter were calculated using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of isotherms.

2.2.2. X-Ray Diffraction Analysis

The X-ray powder diffraction was performed on a Bruker AXS D8 Advance diffractometer with Ni-filtered CuK α radiation over the 2 Θ range of 20 to 80°.

The contents of MgO and MgF₂ were determined by comparing the reflection intensities in the diffraction patterns of the studied samples with those in the diffraction patterns of physical mixtures of MgF₂ and MgO (containing 15, 30, or 70 mol.% of MgO), calcined at 900 °C. The calculations were made using the program Dquant. The XRD reflections at 2 Θ of 36.92°, 42.92°, and 62.29° for MgO and at 2 Θ of 35.21°, 53.48°, and 60.60° for MgF₂ were taken into consideration. Detailed analytical procedures were described in earlier papers [8,9].

2.2.3. Determination of MgF₂ by the Pyrohydrolysis Method

The MgF₂/MgO samples were subjected to pyrohydrolysis to decompose them (in air and steam flow) followed by potentiometric measurements with a fluoride ion-selective electrode to determine the fluoride content in the analyte in TISAB (total ionic strength adjustment buffer) [10].

2.2.4. Measurement of the Specific Volume of the Pellet

The experimental specific volume of the pellet was calculated from the quotient of the pellet volume and mass. The volume of the pellet (25 mm in diameter), its thickness, and weight were determined with an accuracy of 0.0001 cm³, 0.01 mm, and 0.0001 g, respectively [11]. The theoretical volume of the pellet was calculated from the density of the pellet individual components (i.e., KCl, LiCl, RbCl, MgO, MgF₂) and their percentage in the mixture.

The percentage of the void spaces in the pellet was calculated as the 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 in diameter and transferred to the measuring system. The latter consisted of heating plates with a temperature of 400 °C. A 60 kPa pressure was applied to the pellet. A ceramic fitting with a sensor was placed in the center of the quartz plate to monitor the changes in the pellet thickness (reading accuracy: 0.0001 mm). The changes in the thickness were recorded for 3 min and then the pellet was taken out and examined visually.

2.2.6. Measurement of the Mechanical Strength of the Pellet

The mechanical strength of the pellets with the electrolyte was measured using a digital dynamometer FT-50 made by Sauter (Balingen, Germany). A pellet of a 25 mm 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. The mechanical strength of the pellets was expressed in Newton (N).

2.2.7. Determination of Ionic Conductivity

The pellet was placed between two nickel electrodes connected to an ohmmeter (type 41R-chy, Taipei CHY, Taiwan) and inserted between two thin discs made of mica. Such a set was placed between two heating plates (400 °C), where the upper plate was generating a pressure of 60 kPa. The measurement was continued for 3 min and the final value of resistance was recorded. The changes of the pellet thickness were determined at the same time. The specific conductivity was calculated from Equation (1):

$$k = \frac{1}{R} \times \frac{l}{A} [\text{S} \cdot \text{cm}^{-1}], \quad (1)$$

where: R —resistance in Ω ;

l —distance between electrodes in cm;

A —electrode area in cm^2 .

The ionic conductivity of the pellet was calculated after a 3 min measurement, i.e., after reaching a stable value of the resistance and pellet thickness.

3. Results and Discussion

The impregnation of MgO resulted in the samples containing ca. 10 and ca. 25 mol.% MgF_2 . The results of the quantitative analyses are presented in Table 1. In the case of the 10 MF sample, the actual MgF_2 content was a little higher than intended, whereas in that of the 25 MF sample it was a little lower. The values obtained from x-ray diffraction were about 1% lower compared to those from the pyrohydrolytic method.

Table 1. Physical characterization of MgO, MgF_2 , and MgF_2/MgO samples after calcination in air at 500, 600, and 700 °C for 4 h.

Sample Code	MgF_2 Content *, (Pyrohydrolysis) mol. %	MgF_2 Content, (XRD) mol. %	Calcination Temperature, °C	BET Surface Area #, m^2 g^{-1}	Total Pore Volume #, $\text{cm}^3 \text{g}^{-1}$	Average Pore Diameter #, nm
MgO	0	0	500	161	0.29	9.1
			600	164	0.45	22.6
			700	130	0.49	42.3
10 MF	11.7 ± 0.6	10.5	500	43.4	0.17	18.6
			600	52.3	0.28	22.0
			700	51.3	0.35	26.8
25 MF	22.9 ± 1.1	21.8	500	38.9	0.26	26.3
			600	44.7	0.31	27.9
			700	36.9	0.31	29.4
MgF_2	100	100	500	30.7	0.21	21.5
			600	15.2	0.25	36.2
			700	8.6	0.58	56.2

* Error calculated from measurements of three nominally identical measurements. # For the BET surface area, total pore volume, and average pore diameter, the measurement error did not exceed 2.5%

Table 1 also shows values of the surface area determined by the BET method, average pore diameter, and the pore volume calculated by the BJH method on the basis of the desorption branch of isotherms for the samples calcined at different temperatures.

Surface areas of the samples subjected to the impregnation treatment were several times lower compared to bare MgO. The higher the magnesium fluoride content, the greater the reduction in the surface area, which suggests that the reason for such a trend is the deposition of MgF_2 on the surface of magnesia. The surface area of bare MgF_2 calcined at 500 °C is comparable to the surface areas of MgO samples impregnated with MgF_2 . After the calcination at higher temperatures (600 and 700 °C), the surface area of magnesium fluoride decreased rapidly, but this was not observed in the case of the impregnated samples. It was proven in an earlier study [9] that the surface texture in the MgF_2 -MgO system undergoes stabilization compared to that of bare components. We believe that a similar effect occurred in the present case. At the same time, we observed a decrease in the porosity of the samples with an increasing calcination temperature, which is a result of the sintering of narrower pores. For instance, in the case of the 10 MF sample calcined at 500 °C, the average pore diameter was 18.6 nm and after the calcination at 700 °C it increased to 26.8 nm.

The isotherms of low-temperature N_2 adsorption on MgF_2 , MgF_2/MgO , and MgO calcined at 500 °C in air are shown in Figure 1. All the isotherms can be classified as IV(a), according to the International Union of Pure and Applied Chemistry (IUPAC) classification [12], i.e., the type that is characteristic of mesoporous materials. The isotherm measured for MgO calcined at 500 °C exhibits a hysteresis loop of type H2(b), which indicates capillary condensation occurred in the mesopores.

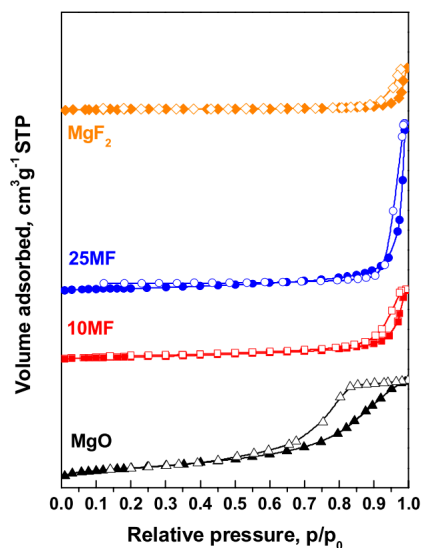


Figure 1. Nitrogen adsorption–desorption isotherms for MgF_2 , 10 MF, 25 MF, and MgO calcined at 500 °C.

Such a shape of the hysteresis loop is characteristic of mesoporous adsorbents containing ink-bottle shaped pores with varied neck sizes. A somewhat different shape of the hysteresis loop occurred in the case of the MgF_2/MgO samples. The nitrogen physisorption isotherm was type IV(a), however, the hysteresis loop of type H1 indicates the presence of wide mesopores. While analyzing the shape of isotherms, one can conclude that the surface of MgO was covered with MgF_2 , because the shape of the isotherms measured for the bare MgF_2 and impregnated samples was similar, whereas that for bare MgO clearly differed from them.

X-ray diffraction patterns (Figure 2) show that in the MgF_2/MgO system calcined at 500 °C, no mixed phase was formed. The studied samples contained only separate phases of MgF_2 and MgO.

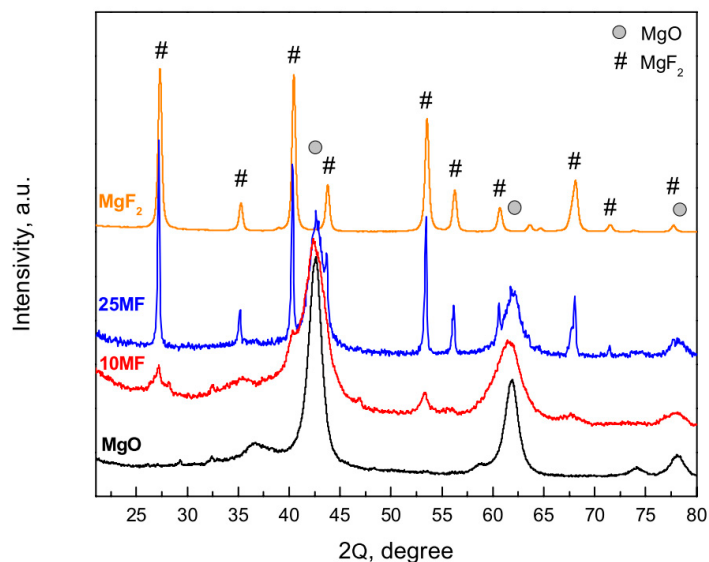


Figure 2. X-ray diffraction patterns of MgO, 10 MF, 25 MF, and MgF_2 samples heated at 500 °C.

The MgF_2/MgO samples were employed as a filler for the preparation of electrolyte-containing pellets in the form of a eutectic mixture consisting of 31.54 wt.% LiCl, 23.47 wt.% KCl, and 44.99 wt.% RbCl. Earlier studies indicated that the most advantageous properties are encountered in the case of pellets containing 40 wt.% of the filler and 60 wt.% of the electrolyte [5]. Thus, we applied the above

filler/electrolyte proportion while studying the electrolyte absorption, mechanical strength, unfilled spaces (voids) in the pellets, and the state of the pellets after cooling. The results of these studies are presented in Tables 2 and 3.

Table 2. Results of the measurements of dimensional stability (S), mechanical strength (MS), and the unfilled spaces (V) in the pellets, when using MgO, 10 MF, and 25 MF as immobilizing agents. The immobilizing agent content in a pellet was 40 wt.%.

Calcination Temperature of the Electrolyte Immobilizing Agent, °C	MgO			10 MF			25 MF		
	S, %	MS, N	V, %	S, %	MS, N	V, %	S, %	MS, N	V, %
500	7.6 ± 0.3	4.12 ± 0.08	47.8 ± 0.4	12.7 ± 0.4	6.49 ± 0.08	49.1 ± 0.4	7.0 ± 0.4	6.02 ± 0.08	48.8 ± 0.4
600	7.0 ± 0.2	3.74 ± 0.08	43.1 ± 0.4	14.9 ± 0.4	5.83 ± 0.08	47.6 ± 0.4	12.7 ± 0.5	5.89 ± 0.08	47.8 ± 0.4
700	6.2 ± 0.2	3.82 ± 0.08	30.0 ± 0.4	20.4 ± 0.5	5.43 ± 0.08	47.5 ± 0.4	70.3 ± 1.1	5.92 ± 0.08	41.6 ± 0.4

Table 3. Photographs of pellets consisting of electrolyte and immobilizing agents: MgO, 10 MF, or 25 MF, calcined at 500, 600, and 700 °C. The amount of electrolyte: 40 wt.%.

Calcination Temperature of the Immobilizing Agent, °C	MgO	10 MF	25 MF
500			
600			
700			

The electrolyte absorption was determined based on the change in the thickness of pellets (%) at the pressure 60 kPa and temperature of 400 °C. The smaller the changes of the above parameter, the more stable the behavior of the electrolyte-containing pellet. From this point of view, the most advantageous was the behavior of bare MgO, in which case the higher the temperature of the initial calcination resulted in a greater stability of the pellets. The introduction of MgF₂ to MgO deteriorated the absorption properties, although the absorption ability of the filler 25 MF calcined at 500 °C was close to that of bare MgO. A particularly large deterioration of absorbability occurred in the MgF₂/MgO fillers calcined at higher temperatures (600 and 700 °C). Regarding the mechanical strength, the addition of MgF₂ clearly improved this parameter (almost twofold). For all the studied samples, a reduction in the mechanical strength was observed when the filler calcination temperature increased. The volumes of unfilled spaces (V%) were similar for all the fillers, however, bare MgO behaved a bit better.

A particularly important parameter for cell operation is the ionic conductivity of molten electrolyte-containing pellets (Figure 3). In this respect, magnesia impregnated with MgF_2 is clearly the best choice. An exceptionally high ionic conductivity was observed for the 25 MF system—it was threefold higher than in the case of bare MgO . The reason for this fact can be the presence of MgF_2 , directly contacting the electrolyte. Additionally, the ionic conductivity increased with a rising filler calcination temperature. However, Table 2 shows that at the same time, the electrolyte absorption declined, which is adverse for the operation of the entire electrolyte–filler system. The exceptionally high ionic conductivity makes it possible to use a greater amount of the filler and to reduce the amount of expensive electrolyte without any deterioration in the operation of the high-temperature cell. This should improve the absorption of the electrolyte and reduce the possibility of its leakage during the operation of the system.

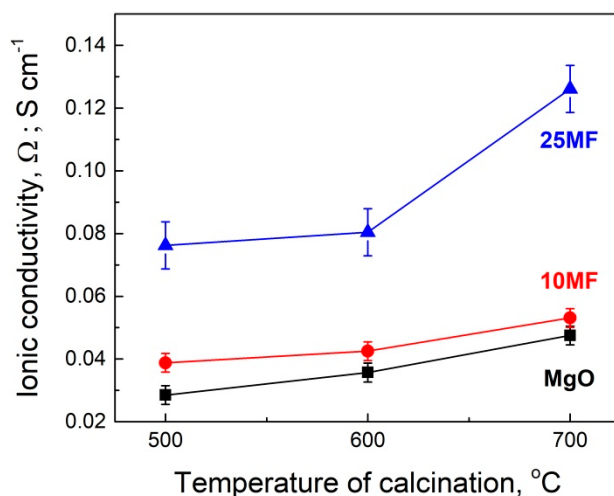


Figure 3. Changes in the ionic conductivity of pellets of the MgF_2 - MgO system, containing 10 and 25 mol.% MgF_2 as a function of the temperature.

The analysis of the pellet state after the electrolyte leakage test (Table 3) indicates the appearance of leakages during the electric tests at 400 °C. In this respect, the tested fillers were similar. The application of fillers calcined at higher temperatures clearly increased the leakage.

In summary, the impregnation of MgO with MgF_2 had a particularly advantageous effect on the mechanical strength and ionic conductivity of the electrolyte–filler pellets. The mechanical strength is of key importance in the process of cell assembly, whereas the increased conductivity of the molten electrolyte reduces the electric power lost during cell operation. An additional asset is that MgF_2 does not absorb CO_2 in contradistinction to MgO , which easily absorbs both carbon dioxide and water. That is why the covering of magnesium oxide with magnesium fluoride protects MgO from hydrolysis and the formation of MgCO_3 on the surface. It should be mentioned that the latter two processes are highly undesirable because at the cell operation temperature, water vapor evolves and magnesium carbonate decomposes. For this reason, we believe that the impregnation of MgO with magnesium fluoride favorably modifies the properties of magnesium oxide used as a filler in high-temperature cells.

4. Conclusions

1. The impregnation of magnesia with magnesium fluoride results in the covering of the MgO surface with MgF_2 .
2. The surface MgF_2 protects MgO against CO_2 , which limits the increase of the internal pressure in the activated cell.

3. The application of the MgF_2/MgO system as a filler in the high-temperature cells considerably improves parameters, such as the mechanical strength and ionic conductivity, of the molten electrolyte in the electrolyte–filler pellets.
4. The MgF_2/MgO system is a promising filler for high-temperature cells.

Author Contributions: M.Z. was responsible for conceptual work, experiment planning and overall care about manuscript writing; A.K. was responsible for preparation of a majority of samples (MgO , MgO-MgF_2 , MgF_2) and determination of MgF_2 by the pyrohydrolysis method (experimentation); M.P. was responsible for determination of the surface area, pore volume, and pore diameter (experimentation and interpretation); B.C. was responsible for the determination of dimensional stability and electrolyte leakage test, determination of ionic conductivity, measurement of the mechanical strength and elaboration of some parts of manuscript; I. T.-F. was responsible for electrolyte immobilizing agent characterization by XRD method and determination of MgF_2 by the XRD method; M.W. was responsible for overall conceptual care about MgO-MgF_2 electrolyte immobilizing agent and elaboration of some parts of manuscript.

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