

# Melt Casting LiFePO<sub>4</sub> II. Particle Size Reduction and Electrochemical Evaluation D. D. MacNeil,<sup>a,\*,z</sup> L. Devigne,<sup>a</sup> C. Michot,<sup>b</sup> I. Rodrigues,<sup>a</sup> G. Liang,<sup>b,\*</sup> and M. Gauthier<sup>b</sup>

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LiFePO<sub>4</sub> was prepared using a melt casting technique of  $Li_2CO_3$  and FePO<sub>4</sub> precursors at 1000 °C. The product was characterized by X-ray diffraction and is of the olivine structure with a minor amount of  $Li_4P_2O_7$  impurity. The synthesis, based on a molten procedure, provides a route to large-scale synthetic practices and reduced cost through the use of inexpensive precursors and short reaction times. The large particle sizes of the LiFePO<sub>4</sub> crystals obtained from the melt casting were reduced to 200 nm by a series of successive milling techniques without affecting the purity of the sample. A subsequent carbon coating on this milled material with a variety of carbon precursors was capable of producing samples with high capacities and electrochemical results similar to that of commercial LiFePO<sub>4</sub> powders. These results indicate that the melt casting procedure could be a competitive synthetic technique for the large-scale production of LiFePO<sub>4</sub>.

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 $\rm LiFePO_4$  has received a large amount of attention as a positive electrode material for lithium-ion batteries.  $^{\rm l-4}$  It represents a low cost, thermally stable, and environment-friendly substitute for cobalt-based lithium metal oxides, which are currently used as cathodes in the batteries of portable computers and cellular phones. In addition, the realization of high power batteries that have large capacity at high rates of charge and discharge is possible with small particle, carbon-coated LiFePO<sub>4</sub>.<sup>5</sup> These properties have led to its consideration as the cathode material for the storage battery of plug-in hybrid electric vehicles.<sup>6</sup> The electrochemical performance of this material is strongly dependent on the synthesis method. Thus far, most commercial LiFePO<sub>4</sub> products are synthesized by the use of solid-state chemistry methods,<sup>7,8</sup>while a large amount of work is devoted to the development of hydrothermally prepared LiFePO<sub>4</sub> due to the smaller particle size obtained through this method.9,10 These two methods have drawbacks in that they either require a lengthy process or costly precursors. In Part I, we introduced a method of LiFePO<sub>4</sub> synthesis that has the capability to provide large amounts of sample from a variety of precursors and a short reaction time.<sup>11,12</sup> This melt casting procedure uses typical metallurgical synthesis methods and can easily provide samples in kilogram quantities. In Part I of this two-part series, we described the synthesis and structural characterization of LiFePO<sub>4</sub> from melt casting and demonstrated that pure LiFePO4 can be obtained from a variety of precursors. We were also able to demonstrate samples with metal substitutions, such as Mn and Mg.

Although the melt casting procedure does provide a pure, electrochemically active material, the large particle size of the synthesized sample results in inferior electrochemical properties, i.e., a low capacity compared to its theoretical value as well as capacity loss with extended charge–discharge cycling. Particle size reduction helps reduce the mass transfer resistance within the LiFePO<sub>4</sub> particle, while a carbon coating improves electrical conductivity. In the present study, we detail the steps involved in the preparation of LiFePO<sub>4</sub> samples from a melt casting process with electrochemical properties that are comparable to those of commercial solid-state and hydrothermally prepared samples of LiFePO<sub>4</sub>. A continuous wet milling procedure is required to efficiently lower the particle size of the melt-cast samples to nanometer dimensions in which good electrochemical properties are possible. Carbon coating the milled

samples with a variety of carbon precursors allows the achievement of a high electrochemical capacity and stability with extended elevated-temperature charge–discharge cycling.

## Experimental

LiFePO<sub>4</sub> samples were prepared by a melt casting process as described in Ref. 12. Briefly, stoichoimetric amounts of FePO<sub>4</sub>·2H<sub>2</sub>O (Buddenheim KG, Germany) and Li<sub>2</sub>CO<sub>3</sub> (Limtech, Québec) were combined with 25 mol % of graphite powder (Timcal, Belgium). The mixture was then placed in a graphite crucible and heated to 1000°C under an Ar flow for 1 h. After cooling to room temperature, the sample was broken with a hammer. A rough grinding was performed with a disk mill (Retsch DM 200). The disk-milled material (particle size  $\sim 100 \ \mu m$ ) was then placed in a planetary mill (Fritsch) with a 5 times excess of isopropyl alcohol (IPA) for suspension. The planetary mill used a 250 mL Syalon container with three 25 mm Syalon balls. A 90 min milling procedure was performed. The sample was then collected and further processed in a continuous-flow agitator bead mill (MiniFer by Netszch). The milling procedure consisted of preparing a 20% (by weight) suspension of LiFePO<sub>4</sub> in IPA. This solution was then passed through the mill containing 140 mL yttria-stabilized zirconia grinding media operating at a speed of 1500 rpm. Two different sized media were used for milling: (i) 0.7–0.9 mm beads (nanomill no. 1) and (ii) 0.5–0.7 mm beads (nanomill no. 2 and no 3). The mill ran continuously until a stabilized particle size was obtained. The particle size was continuously monitored during the milling procedure by the use of a Horiba particle size analyzer (LA 300). After particle size stabilization, the sample was collected from the mill and kept in suspension until further use.

Carbon-coated LiFePO<sub>4</sub> samples were prepared by dissolving a carbon precursor in either IPA or H<sub>2</sub>O. The precursors used in this paper were  $\beta$ -lactose, L-ascorbic acid, poly(maleic anhydride-*alt*-1-octadecene) (PMAAO), salicylic acid, and hydroxyethyl cellulose. The carbon precursor suspension was then added to the LiFePO<sub>4</sub> suspension and the mixture was allowed to evaporate to dryness. The powder was then heated to 700°C for 1 h under a N<sub>2</sub> flow. X-ray diffraction (XRD) was performed with a Bruker D8 Advance equipped with a Cu X-ray tube and a diffracted-beam monochromator. Scanning electron microscopy (SEM) micrographs were carried out with a Hitachi S-4300 microscope. Chemical analysis was performed with a Fisons Instruments (SPA, model EA1108) elemental analyzer to determine the C, H, N, and S concentration within the sample.

Commercial carbon-coated LiFePO<sub>4</sub> samples were obtained from Phostech Lithium, Inc. Samples of both energy grade (P1) and

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Figure 1. (Color online) XRD of LiFePO<sub>4</sub> after (a) disk milling, (b) planetary milling, and (c) nanomilling. Indicated peaks on scan (a) are from a minor impurity of  $Li_4P_2O_7$ .

power grade (P2) LiFePO<sub>4</sub> were provided and used as received. The energy grade product, P1, was produced following a solid-state synthesis method described in Ref. 14, while the power grade product, P2, was produced via a hydrothermal synthesis method described in Ref. 15. Electrochemical evaluation of the nanomilled and commercial samples was performed by combining 11% of a conductive carbon (Timcal EBN1010) and 7% polyvinylidene difluoride [3.3% in *n*-methyl pyrrolidone (NMP)] with the electrode powders. An extra portion of NMP was added to the mixture to form a slurry, which was then mixed overnight in a roller mill. The slurry was then coated on a piece of carbon-coated Al foil. The electrode was dried overnight at 60°C under vacuum. The next day, 13 mm diameter disks were punched for cell assembly in standard 2032 coin-cell hardware (Hohsen) with a single lithium-metal foil used as both counter and reference electrodes. Cells were assembled in an argonfilled glove box with 1 M LiClO<sub>4</sub> in ethylene carbonate (EC)/ dimethyl carbonate (1/1) (Ferro) or 1 M LiPF<sub>6</sub> in EC/diethyl carbonate (3/1) (UBE) as the electrolyte. Electrochemical evaluations were performed with a VMP electrochemical station (Biologic, France). The cells were either evaluated for rate capability (with LiClO<sub>4</sub> electrolyte at room temperature) or for 60°C chargedischarge cycle stability (with LiPF<sub>6</sub> electrolyte). A sequence of discharging the cell at a C/12 rate and then sequentially up to 10C following a C/4 charge was used to test the rate capability of the sample. The charge-discharge cycling stability tests were performed by charging and discharging between 2.2 and 4 V at a rate of C/4 at 60°C. After 10 cycles at C/4, one C/8 charge-discharge cycle was performed to test the low rate performance of the cell, after which the C/4 sequence was repeated.

# **Results and Discussion**

Figure 1 presents the XRD patterns of the LiFePO<sub>4</sub> sample after various milling procedures. The main reflections in all samples can be indexed on an orthorhombic olivine-type structure with the *Pnma* space group. There is a small amount of  $Li_4P_2O_7$  impurity in the disk-milled sample. The sharp diffraction peaks in the disk-milled sample are indicative of a highly crystalline product. In fact, the sample after synthesis shows large green crystals that can extend over several centimeters. It is clear from the width of the diffraction peak and the loss of diffraction intensity in Fig. 1 that, through the various milling procedures, the crystallite size diminishes. An analy-

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**Figure 2.** SEM micrographs of LiFePO<sub>4</sub> from a melt casting synthesis of (scale bar dimension indicated in brackets) (a) disk-milled product (20  $\mu$ m), (b) planetary-milled product (20  $\mu$ m), (c) nanomilled product with 0.7–0.9 mm grinding media (1  $\mu$ m), and (d) nanomilled product with 0.5–0.7 mm grinding media (2  $\mu$ m).

sis using Scherrer's formula gives an average crystallite size of 99 nm for the disk-milled sample, 98 nm for the planetary-milled sample, and 60 nm for the nanomilled sample. Also, during the various milling procedures there is no introduction of new impurity species compared to the original synthesized material.

The size and morphology of the LiFePO<sub>4</sub> particles were investigated by SEM. Figure 2 shows the micrographs of the LiFePO<sub>4</sub> sample after different milling procedures. The disk-milled product (Fig. 2a) contains large rectangular crystallites with well-defined and smooth faces. As this product is milled in the planetary mill (Fig. 2b), the large crystallites get reduced and the morphology of the crystals becomes more jagged and less defined. There is an overall particle size reduction, but it comes mainly from the destruction/ milling of the larger particles while the small particles remain largely untouched. During the nanomilling process (Fig. 2c and d) the large crystallites get reduced to smaller particles, whose final particle size is dependent on the media size used during the milling procedure. The final milled samples contain a few large particles of 1-2 µm and many smaller submicrometer-sized particles. The morphology for the nanomilled samples is similar and consists of irregularly shaped particles with sharp facets, which clearly demonstrates the grinding process on the particles during the milling procedure. Throughout the milling procedure, the particle size was continuously monitored by laser diffraction. There was a clear decrease in particle size with milling time until a point where the particle size stabilized due to the loss of grinding capability of the media. At this point, the milling operation was terminated and the sample was collected. The particle size analysis of the final milled samples is shown in Fig. 3. The particle size of the starting disk-milled sample (average particle size  $\sim\!100~\mu m)$  was reduced initially to  $\sim\!10~\mu m$ through planetary milling and then to  $\sim 400$  or  $\sim 200$  nm during the wet milling procedure, with the smaller sized media (0.5-0.7 mm)giving the smallest particles. Further particle size reduction is likely possible with the use of smaller milling media. The nano- and planetary-milled samples, which are represented in Fig. 3, were used for further electrochemical evaluation. It is clear that as the sample is nanomilled with smaller media (0.5-0.7 mm), the average particle size is reduced and the particle size distribution significantly improves. This results in a sample that is much more homogeneous. Particle size reduction is an important characteristic for the achievement of good electrochemical performance from LiFePO4 as the material has a very low intrinsic ionic conductivity.

Another important aspect for the development of  $\text{LiFePO}_4$  with high power capabilities is the production of an effective carbon coating on the surface of the  $\text{LiFePO}_4$  particles. The carbon coating



Figure 3. (Color online) Particle size analysis of the various  $LiFePO_4$  samples under study: (a) Disk milled, (b) planetary milled, (c) nanomilled no. 1, (d) nanomilled no. 2, and (e) nanomilled no. 3.

significantly improves the electrical conductivity of the material. In this evaluation, several carbon precursors were tested. Table I provides a list of the precursors, the added concentration, and the resultant carbon content of the sample after heating to 700°C for 1 h under a N<sub>2</sub> atmosphere. The morphologies of a select number of samples are shown in Fig. 4; similar results are obtained from the other samples but are omitted from Fig. 4 for clarity. In Fig. 4a and b, nanomilled samples heated to 700°C without a carbon precursor are shown. They clearly demonstrate that heating the nano-LiFePO<sub>4</sub> material at an elevated temperature in the absence of a carbon precursor causes particle growth of a sample. The size of the heated particles has increased almost 100 times from its precursor. There is no doubt that the electrochemical characteristics of this particle would be insufficient for application as a battery material. In comparison, the samples, shown in Fig. 4c-f have a particle size roughly equal to that of the precursor LiFePO<sub>4</sub> milled material shown in Fig. 2. The particle size deduced from Fig. 4 suggests that the process of carbon coating LiFePO<sub>4</sub> does not significantly change the particle size of the underlying olivine material. A nano-LiFePO<sub>4</sub> sample coated with a carbon precursor inhibits the particle growth that normally occurs during high temperature annealing (Fig. 4a and b). In addition, the process of carbon coating smooths out the morphology of the nanomilled samples to produce particles with a much more uniform circular shape. This variation in morphology is seen via a change in the surface area of the material. The pre-carbon-coated nanomilled LiFePO<sub>4</sub> sample has a surface area of 12.2  $m^2/g$ , while the carbon-coated material has a surface area of 8.2  $m^2/g$ .

	Carbon precursor	Precursor amount (%)	[Carbon] after heat (%)	Rate capability (capacity at indicated discharge rate, mAh/g)					60°C cycling at C/4		
LFP milling procedure									Discharge capacity		
				C/12	С	4C	10C	20C	Initial (mAh/g)	Cycle 40 (mAh/g)	Calculated capacity loss for 100 cycles (%)
Planetary mill	β-Lactose	5	1.1	113	82	60	40	23	121	98	61
	L-Ascorbic	5	1.0	103	73	50	30	0	103	81	56
	PMAAO	5	0.6	108	74	52	34	13	112	81	77
	Hydroxyethyl	-	0.0	100			20			01	
	cellulose	5	0.7	108	71	47	30	0	111	91	56
	Salicylic	5	0.9	58	29	18	9	0	53	32	81
Nano 1 (0.7–0.9 mm)	Salicylic	5	0.6	151	123	82	46	20	155	143	19
	PMAAO	5	0.9	142	120	89	66	35	150	144	9
	Hydroxyethyl cellulose	5	0.8	150	129	92	52	15	153	146	12
Nano 2 (0.5–0.7 mm)	β-Lactose	5	1.3	152	138	116	90	58	156	148	14
	L-Ascorbic	5	1.1	154	140	116	83	35	149	144	11
	PMAAO	5	0.9	149	134	109	78	34	154	148	11
	Hydroxyethyl cellulose	5	0.9	153	139	115	88	51	161	158	6
	Salicylic	5	0.9	151	135	108	78	43	158	152	10
Nano 3 (0.5–0.7 mm)	PMAAO	5	0.7	149	134	105	67	17	153	151	5
		10	0.9	151	140	112	78	36	156	152	6
		15	1.3	149	136	111	85	47	155	149	7
	Salicylic	5	1.0	152	138	109	75	38	158	150	13
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	10	1.0	149	132	105	79	48	157	149	13
		15	1.5	150	138	116	93	63	157	150	10
	Hydroxyethyl cellulose	5	1.4	150	138	110	78	25	158	150	13
		10	1.8	151	138	112	88	65	156	153	9
		15	2.4	156	142	121	98	68	155	152	7
	<b>B</b> -Lactose	5	1.1	156	143	122	101	65	159	152	10
	1-	10	2.0	151	138	116	90	59	158	153	7
		15	3.0	142	126	103	77	47	153	152	2

# Table I. Summary of experimental results on melt-cast LiFePO<sub>4</sub>.



**Figure 4.** SEM micrographs of carbon-coated LiFePO<sub>4</sub> (scale bar indicated in brackets): (a) Uncoated nanomilled no. 1 product heated to 700°C (10  $\mu$ m), (b) uncoated nanomilled no. 2 product heated to 700°C (10  $\mu$ m), (c) PMAAO-coated planetary-milled product (5  $\mu$ m), (d) PMAAO-coated nanomilled no. 2 product (5  $\mu$ m), (e) hydroxyethyl-cellulose-coated planetary-milled product (5  $\mu$ m), and (f) hydroxyethyl-cellulose-coated nanomilled no. 2 product (5  $\mu$ m).

Figure 5 presents the rate capability of the PMAAO-coated LiFePO<sub>4</sub> material at various discharge rates, milling conditions, and carbon coating amounts. It is clear that as the particle size of the molten product is reduced, the capacity that is obtained at higher discharge rates increases due to the improvement in electronic and ionic conductivity within the particle. In addition, LiFePO<sub>4</sub> particles with the same primary particle size but with higher carbon coating concentrations show larger capacities at higher discharge rates due to the improvement of electrical conductivity. This demonstrates the importance of the optimization of the particle size of the product for its specific application, be it for energy density or for power appli-



Figure 5. (Color online) Rate capability of PMAAO-coated  $\text{LiFePO}_4$  samples from various milling conditions and carbon-coating content. Stars: planetary mill; cross: nanomill no. 1 diamonds: nanomill no. 2, squares: nanomill no. 3, 5%, circles: no. 3, 10%, and triangles: nanomill no. 3, 15%.



Figure 6. (Color online) Capacity vs cycle number of PMAAO-coated LiFePO<sub>4</sub> samples from various milling procedures and carbon contents. Cycling was performed at  $60^{\circ}$ C at a discharge rate of C/4 for 10 cycles, followed by one cycle at C/8. Stars: planetary mill; cross: nanomill no. 1 diamonds: nanomill no. 2; squares: nanomill no. 3 5%, circles = nanomill no. 3, 10%; and triangles: nanomill no. 3, 15%.

cations. An application requiring high energy density but lower power could utilize a larger particle size melt-cast material with a lower carbon content, while a high power application would require a smaller particle sized material with higher carbon content. This optimization can be easily performed with the melt-cast LiFePO<sub>4</sub> synthesis by the choice of a correct grinding media size for the desired particle size of the product and carbon concentration for the coating. Table I provides a summary of the rate capability results for all materials and carbons tested in this evaluation. Overall, the trend reported in Fig. 5 for the PMAAO-coated sample (increasing capacity with smaller particle size and increasing carbon coating content) is followed by all carbon precursors investigated to date.

The 60°C discharge capacity with extended charge/discharge cycles of the PMAAO-coated samples are shown in Fig. 6. The test was run at a cycling rate of C/4. After 10 cycles one run at C/8 was performed to test the effect of cycling lifetime on the low rate performance of the cell. It should be emphasized that this test was performed at 60°C, a temperature at which a poor LiFePO<sub>4</sub> material shows rapid capacity loss even though performance at room temperature could appear adequate. In Fig. 6, it is clear that the planetary-milled sample shows a significant drop in capacity (125 mAh/g) compared to the theoretical value of LiFePO<sub>4</sub> (170 mAh/g). Similarly, there is a large rate of capacity loss [77% (calculated) after 100 cycles] with increasing cycle number. This rapid capacity loss with increasing charge/discharge cycles is likely due to the cracking of the large particle ( $\sim 10 \ \mu m$ ) during repeated cycling. This cracking causes the destruction of the carbon coating, which leads to a loss of capacity. Similarly, this cracking likely leads to the loss of contact with the current collector, effectively eliminating the particle from possible electrochemical activity. In comparison, the nanomilled samples have capacities as high as 95% of the theoretical capacity for LiFePO4 and exhibit excellent capacity retention. The difference in capacity obtained by the two nanomilled samples (0.5–0.7 mm media vs 0.7–0.9 mm media) is mainly due to the particle size of the active material that is a result of the chosen size of milling media, where the smaller particle sized material (smaller milling media) obtains a higher capacity. In addition, when the carbon content of a particular milled sample is evaluated, the optimal carbon precursor concentration can be determined. It is important to emphasize that the total weight of the carbon-coated



Figure 7. (Color online) Comparison of commercial energy grade LiFePO<sub>4</sub> (P1, cross), power grade LiFePO<sub>4</sub> (P2, squares), and nanomilled melt-cast LiFePO<sub>4</sub> samples (circles).

LiFePO<sub>4</sub> sample is used to calculate the capacity. The optimal carbon precursor content is consistently 10% for the samples analyzed here. The 10% precursor concentration leads to a carbon coating of roughly 1–2% after treatment at 700°C for 1 h under a N<sub>2</sub> atmosphere. When the carbon precursor is lower or higher than 10%, there is a drop in discharge capacity due to low conductivity (5% added precursor) or large inactive carbon concentration (15% added precursor). A summary of all the capacity retention results is presented in Table I.

Figure 7 compares the rate capability of two commercially available LiFePO<sub>4</sub> products from Phostech Lithium to one of our best performing nanomilled melt-cast LiFePO<sub>4</sub> samples. All cells were prepared and analyzed the same way with the same equipment. The two commercial samples are optimized for specific applications, either energy density (P1) or power density (P2). More information on these products can be found elsewhere.<sup>14-16</sup> It is clear from Fig. 7 that the nanomilled melt-cast sample compares very well to commercial samples. These samples were prepared using laboratory methods and were not optimized for rate capability. Higher capacities are likely when commercial cells and coating practices are used for these samples. The coating methods used and the cell testing methods demonstrate a baseline of performance for these materials.

Figure 8 compares the extended charge/discharge capacities of the commercial samples with those of the best nanomilled melt-cast samples. It is clear that the commercial samples have a significantly improved capacity retention ability (1–2% calculated loss over 100 cycles) when compared to the nanomilled samples ( $\sim 7\%$  calculated loss over 100 cycles), but the nanomilled samples have larger capacity numbers, which may be the result of a lower amount of carbon coating. It should be emphasized that the milling procedure was limited due to the available milling media size. Smaller milling media should result in smaller sized LiFePO<sub>4</sub> and improved capacity retention ability.

The results in Fig. 7 and 8 clearly demonstrate that melt-cast, milled, and carbon-coated LiFePO<sub>4</sub> is capable of providing an electrochemical performance similar to that of commercial material. The results shown here are from experimental samples and have not been optimized for powder processing; this is a very important part of the technique to produce dense electrode films for commercial cells. For example, the tap densities of commercial LiFePO<sub>4</sub> powders are 1–1.1 g/mL for P1, and 0.6–0.7 g/mL for P2, while the experimental powders shown in Fig. 7 and 8 have tap densities of 0.8–1 g/mL. Further work is required on the nanomilled samples to produce elec



**Figure 8.** (Color online) Comparison of capacity vs cycle number of commercial energy grade LiFePO<sub>4</sub> (P1, cross), power grade LiFePO<sub>4</sub> (P2, diamonds), and two nanomilled melt-cast LiFePO<sub>4</sub> samples (circles, squares). Cycling was performed at  $60^{\circ}$ C for 10 cycles at C/4, followed by one cycle at C/8.

trode films of high density for such applications as electric vehicles. Ultimately, we are searching for methods to increase tap density and lower the surface area of the carbon-coated LiFePO<sub>4</sub> material, such that high electrode density films could be produced from these melt-cast materials.

### Conclusion

 $LiFePO_4$  was obtained from a molten process (1000°C) that has shown, with the proper milling procedure, the ability to obtain high capacities (95% of theoretical capacity) with excellent cyclability and rate capability. The electrochemical characteristics compare favorably with those of commercially available material. It is crucial that, with this synthetic approach, the optimal milling procedure is obtained. We are continuing our investigation with smaller media with the goal of decreasing particle size below 200 nm. With a significantly lower reaction dwell time at high temperature, the ability to use inexpensive precursors, and ease of scale-up compared to other synthesis methods employed in the literature, it is believed that the melt casting method to synthesize LiFePO<sub>4</sub> will have a very important role in the future development of LiFePO<sub>4</sub> applications. The method offers the promise of pure, low cost, and large-scale sample production for use as high power hybrid electric vehicles and plug-in hybrid electric vehicle applications. In addition, further work is currently being performed on the development of LiMPO<sub>4</sub>, where M = Mn, Co, Ni, or a combination thereof, as well as the optimization of powder characteristics such that dense electrode films can be produced.

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