Deflagration Products from Emulsion Explosive
Unconventional nano-powders from ion reaction

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Abstract. The present situation of detonation synthesis and emulsion explosives is summarized. To solve the problems in research for lithium ion batteries, we suggested that zinc and lithium oxides should be used as cathode materials for lithium ion batteries. So, we design unconventional emulsion explosives, and synthesize zinc and lithium oxides by means of deflagration firstly. Also, microstructures and morphology of nanometer thin sheets in the deflagration soot of emulsion explosives are measured in our experiments; namely, we surveyed and analyzed products with the implement of XRD, TEM and FTIR. It is concluded that nanoparticles of lithium and zinc oxides can be synthesized through deflagration of the unconventional emulsion explosive. Main contents and research results are as follows: First, unconventional emulsion explosives for synthesis of zinc and lithium oxides are designed firstly, and we also discuss mechanics of deflagration. In the final analysis, we succeeded in synthesizing nano-sheets of zinc and lithium oxides by deflagrating at the fist time. Second, we tested microstructures of nanometer thin sheets of lithium and zinc composite oxides. Third, by contrast to industrial emulsion explosives, we analyzed the deflagration mechanics of the unconventional emulsion explosives. Last, zinc and lithium nanooxides are successfully collected and validated by XRD, TEM and FTIR exactly.

1. Introduction
A zinc and lithium composite oxide is the subject of growing interest for different applications in electronic components [1-4]. Especially, G.Ceder regarded that LiZnO2 compound has a higher voltage than that of LiCoO2 [5]. More recently, it was reported that these oxides nanomaterials have generated tremendous interests in both the scientific and engineering community, which has visibly led to rapid and intense growth in research focus [6-13].

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In this paper, we report the synthesis of nanometer sheets of composite oxides, which we believe, has never been reported. We can grow these nanoscale structures in a cheap manner through the addition of nitrates using the emulsion explosive deflagration process. This novel method allows us to synthesize nanometer composite oxide sheets. Jianjun Liu et al [14] thought that the shock-induced chemical reactions leading to synthesis of compounds in powder mixtures occurred under conditions of the microsecond-scale duration of the high pressure, stress, strain-rate, and temperature states. Such high-rate chemical reactions can be advantageously utilized to synthesize materials with novel phases and unique microstructures, or to generate radically modified materials with physically interesting or technologically useful properties. I.J. Davidson [15] reported that using solid-state reactions method, usually, the powder preparation route is also quite complicated, for example, several times calcination and subsequent physical grindings. Moreover, its electrochemical properties are greatly dependent on its crystalline particle size [16].

Until now, there are a few reports concerning zinc and lithium composite oxide synthesized by deflagration of emulsion explosives, which is a kind of promising technique for synthesis of lithium transition metal oxide cathodes. Here, for the first time, zinc and lithium composite oxide was synthesized from LiNO$_3$ and Zn(NO$_3$)$_2$·6H$_2$O by using fast chemical reaction.

2. Experimental

The emulsions were prepared using a simple facility consisting of a thermostat and a container equipped with a stirrer. The solution of oxidizers was heated to 105°C and then slowly added to the container, in which a preheated (90°C) mixture of fuels (oil and paraffine) with the emulsifier was agitated with the stirrer at a speed of 800 rpm. After adding the entire amount of the oxidizer, the agitation was continued for about three minutes to obtain fine particles of the emulsion matrices.

The explosive charges were put into a thin plastic bag with an approximate 1330 kg/m$^3$ density and the mass was fixed at 0.800 kg of explosive matter. For each charge an electric No.8 initiator and a 0.038 kg plastic RDX booster were used. The deflagration experiments were performed in an explosive chamber (shown in Fig. 1). This method provides a very fast quenching space. The air surrounding the charge provides efficient cooling of deflagration products and thus reduces the reuniting of obtained nanoparticles. The deflagration experiments were done in a steel tank of 14.1 m$^3$. The explosive charge was placed in a polyethylene bag, which was suspended at the tank center. The deflagration products contained some impurities such as fragments from the tank walls (Fe$_2$O$_3$, Al$_2$O$_3$), copper and steel from the detonator, and PE from the bag and the leg wires of the detonator. Large size impurities were eliminated by simple filtration of the suspension. The solid residue was washed thoroughly and dried. All the final products were analyzed by XRD ($\lambda$CuK$\alpha=1.5406$ Å). So for all the experiments, the deflagration of emulsion explosives synthesized a black powder containing mainly ultradispersed composite oxides of zinc and lithium composite oxide.
The deflagration soot was then studied by use of X-ray diffraction (XRD). Scanning electron microscopy (SEM) analysis was performed with JEDL JEM-1200EX (Japan) for deflagration synthesized Lithium zinc oxides. XRD analysis was carried out on an XRD-6000 Shimadzu (Japan) diffractometer using Cu Kα irradiation with input power of 50 kV and 150 mA. The divergence slit angle, scattering slit angle and receiving slit height were selected as 2, 2°, and 0.3 mm. The diffraction intensities were measured every 0.028 step for 1 s in the wide 2θ range from 10 to 100° at room temperature (293 K). After sintered at 600℃ for 1 hour, the shape and size of the as-obtained particles were observed by transmission electron microscope (TEM, Tecnai G2 20 S-twin).

3. Results & Discussion

3.1. X-ray diffraction (XRD) analysis

The exact mechanism of the formation of such nano-grains in the emulsion explosive derived so far is poorly understood. Fig. 2 shows the XRD patterns of the dynamically synthesized zinc and lithium composite oxide. We obtained a nanosized diamond texture containing zinc and lithium composite oxide. It is obvious that the Bragg reflection peaks of the dynamically synthesized zinc and lithium composite oxide are broadened, which may result form small grain size and/or presence of microstrain. Here the mean grain size for deflagration synthesized zinc and lithium composite oxide refers to the mean size of crystallites of crystalline particles. XRD analyses were conducted at a fixed temperature in the present study; a precise determination of the structural parameters need more experiments including both high temperature and low temperature experiments. Explosive deflagration is nonequilibrium processes, generating a short duration of high pressure and high temperature.
The structures for the solid solutions were identified by means of powder X-ray diffraction (XRD) on an XRD-6000 diffractometer with Cu Kα radiation at room temperature. The average grain size (D) was measured from the XRD peak using the Scherrer formula [10]:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda = 0.15406 \text{ nm} \), \( \theta \) is the diffraction angle of the most intense peak, and \( \beta \) is defined as the experimental half-width.

The calculated mean grain sizes were 51.42 nm for deflagration synthesized zinc and lithium composite oxide. Here the mean grain size for deflagration synthesized zinc and lithium composite oxide refers to the mean size of crystallites of crystalline particles.

3.2. Analysis of TEM

A distinguishing feature of emulsion explosives is that in the aqueous solution, the lithium nitrate, zinc nitrate and ammonium nitrate are present in the form of tiny droplets covered with a very thin fuel layer. As a result, the interfacial surface of the emulsion is very large, the unconventional emulsion explosive in a higher density can be deflagrated completely when initiated.

Fig. 3 (a) and (b) are morphologies by TEM. Transmission electron microscopy was used to characterize the products. Zinc and lithium composite oxide with smaller primary sheets of widths from 50 to 100 nm, thickness 5 nm, and a variety of morphologies were found.

Although TEM picture shows smaller particles, which are aggregated further to form agglomeration, varied sizes, it is necessary to obtain the information regarding smallest primary particles. For this purpose, the TEM study and selected area electron diffraction (SAED) were shown in Fig 3. The SAED pattern of lithium and zinc oxide nanometer sheets shows a clear diffraction ring and varied points corresponding to the crystal planes of phase.

P.W. Chen et al [17] regarded that due to the active surface and strong adsorption activity, UFD particles were aggregated into clusters of dimensions from hundreds of nanometers to several micrometers. The clusters could exhibit round or polyhedral shapes. Highly dispersed and stabilized suspensions of UFD could be obtained through selecting the appropriate liquid
media and dispersing agents. UFD surface was covered by a large amount of carbonyl, carboxyl, methyl and nitryl groups. UFD was characterized by having considerable microstress and larger crystal lattice parameters than bulk diamond. Such a high level of lattice deformation could be explained either by the inhomogeneous deformation of UFD particles during the strongly non-equilibrium deflagration process, or by the effect of other inserted atoms in the crystal lattice. The value of UFD microstress did not change noticeably when the UFD was heated up to 1000°C in an Ar atmosphere, which can be explained by the high potential barrier hindering the annealing of defects.

Troyanov et al [18] reported that for a mixture of 20% gibbsite and 80% hexogen the theoretical temperature of the explosion is about 2000°C. Hexogen C3H6N6O6 decomposes into CO2, CO, H2O, H and N under explosion. The positive oxygen balance governs the sufficient supply of oxygen in the final effluxes of the explosion.

### 3.3. Infrared Analysis

The Fourier-IR spectrum Fig. 4 shows that the sheet surface was covered by a large amount of carbonyl, carboxyl, methyl and nitryl groups. Due to this fact, it was possible to chemically modify the sheet surface. The synthesis and purification conditions could have affected the type and amount of groups on the surface of sheet. The presence of these functional groups could cause the deviation of the lattice parameter and the density of sheet from the corresponding values for normal oxide crystals. Due to the active surface and strong adsorption activity, lithium and zinc oxide particles were aggregated into clusters of dimensions from hundreds of nanometers to several micrometers. The clusters could exhibit sheet polyhedral shapes. Highly dispersed and stabilized suspensions of sheet could be obtained through selecting the appropriate liquid media and dispersing agents.

### 4. Conclusions

The zinc and lithium composite oxides with a thin sheet structure formed after deflagration wave treatment due to the high quenching rate are different from that of the normal combustion products. It might also provide a cheap large-scale synthesis method. Explosive deflagration is strongly nonequilibrium processes, generating a short duration of high pressure and high temperature. Free metal atoms are first released with the decomposition of explosives, and then these metal and oxygen atoms are rearranged, coagulated and finally crystallized into zinc and lithium composite oxide during the expansion of deflagration process. For emulsion explosive deflagration, the pressure, the temperature and the adiabatic gamma were lower than those of deflagration process, but higher than those of combustion or sintering processes. The inherent short duration, high heating rate and high cooling rate prevent the zinc and lithium composite oxide crystallites from growing into larger sizes and induce considerable lattice distortion.

We can control the morphology and composition of zinc and lithium composite oxide by using deflagration of the unconventional emulsion explosives. The nanoagglomerations, and high surface area of these unique nano structures make them a potential candidate of cathode active materials for Lithium ion batteries.
Figure 3 TEM image of deflagration synthesized lithium and zinc oxides.

Figure 4 Infrared image of deflagration synthesized lithium and zinc oxides

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