Enhancement by mechanochemistry of materials performances for energy storage and catalysis.

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Since the early sixties, mechanochemistry, which is a room temperature process using mechanical energy to obtain highly homogeneous mixtures in which each compound is in a very highly divided and reactive state, has been of great interest for the preparation of either amorphous or crystalline nanometric powders. The positive attributes of such technique within the field of energy storage or catalysis will be illustrated from examples taken from our group.

Our first example dwells with the field of catalysis and more specifically with the synthesis of lithiated manganese oxides by ball-milling a mixture of Li_2O and MnO_2. Such mechanosynthesized Li-Mn-O oxides display outstanding catalytic activity. Indeed, a remarkable decrease of 200 °C (from 650 °C to 450 °C) in the carbon black combustion temperature and a 100 % toluene conversion rate for a temperature lower than 200 °C were noted [1]. Similar enhancement of the catalytic activity was found for perovskite-type oxides emphasizing the benefit of mechanochemistry in this field.

The second example deals with the effect of mechanical grinding on soft and hard carbons, used as negative electrode in lithium batteries. Optimized carbonaceous material for batteries applications (i.e. materials having a reversible capacity of 1.7 Li for Li_xC_6 with 33 % of irreversible capacity) were prepared by shock-type grinding. In contrast, shear-type grinding leads to carbons exhibiting specific surface area as high as 700 m^2/g having a double layer capacitance of 62 F/g. Furthermore, we experience that such performances are strongly affected by the type of grinding atmosphere. Low oxygen pressure in the grinding medium will induce a decrease in cell polarization while maintaining the electrochemical performances whereas an increase in oxygen or hydrogen content lead to an increase in capacities and double-layer capacitance. For instance under 10 bars of oxygen, a double-layer capacitance of 120 F/g was obtained, in basic media, for a carbonaceous compound exhibiting a 5 m^2/g BET specific surface area.

The importance of enhanced surface area and disorder state provided by ball milling will be further illustrated in the case of hydrogen-absorbing alloys. Enhancement of the mechanosynthesized AB_5 multielement alloys electrochemical activity in Ni/MH battery was achieved by the elaboration, by grinding, of a alloy-carbon composite [3]. During grinding of the alloy and carbon, cumulative positive effects are taking place : 1) the dispersion of fine carbon particles around the alloy enables a better intergranular conductiviy 2) the reducing role of carbon prohibiting the oxide coating on AB_5 particle enabling a better hydrogen reversible sorption, and 3) the agglomeration of the broken graphen layers around the alloy surface that may prevent from surface oxidation. A similar approach was successfully applied to promote the hydriding/dehydriding performances of Mg based alloys. Further improvement of the hydrogen sorption of mechanosynthesized MgNi alloys from both kinetics and capacity aspects was achieved when combining the mechanical treatment with graphite with the deposition of Pd particles on the alloy surface via a chemical process. Hydrogen release as high as 2.5 % in weight at 150 °C was obtained [4].

In summary, in this work we will show through several examples how one can modify and enhance material properties by using mechanochemistry. The key role of the disordered nature and more specifically of the surface on the improvement of the ground material performances will be emphasized by showing the benefit of surface treatments.

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