Effect of Ionic Liquid on the Formation and Stabilization of MnO_2 Nanoparticles

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***Abstract*—Due to their nanometric dimensions and crystal structures, manganese dioxide MnO_2 nanoparticles (NPs) are of interest in various fields. The electrochemical reactivity of manganese dioxide MnO_2 generally depends on its crystal structure which depends on the conditions of its synthesis.**

Nanoscale MnO_2 has physical and chemical properties, on the borderline between molecular state and massive state. With the reduction in size come new properties. In all cases, a significant increase in the specific surface is observed. We can therefore have new properties, which are not observed in the macroscopic material. These properties can be catalytic, magnetic, optical, etc.

Here and in a work carried out in the synthesis and catalysis laboratory, we have synthesized NPs of manganese dioxide (MnO_2) with a simple method and using an ionic liquid (IL) as the reaction medium. The results we obtained clearly show the effect of IL on the sizes of the crystallites obtained. Indeed, by comparing the XRD spectra of our samples with those of the crystallites synthesized without the use of IL, we notice that the use of IL in the synthesis considerably reduces the sizes of the crystallites.

IL plays several very interesting roles in the formation and stabilization of NPs.

***Index Terms*—Ionic liquid, Nanoparticles, Sonochemistry.**

I. Introduction

We have three different types of battery; saline batteries of the Leclanché type, example: (Zn/MnO_2 with NH_4Cl as electrolyte), alkaline batteries whose electrolytes are alkaline solutions (NaOH, LiOH) and button cells in which the manganese oxide MnO_2 is replaced by another oxide Ag_2O [1]. A (Zn/MnO_2) type cell represents a system which produces electrical energy upon contact with a consumer. This process is irreversible, that is to say that the raw materials will not be reusable after using their energy.But according to an analysis carried out by the group of N. BENCHIHEUB, by X-ray diffraction on the recycled MnO_2 powder shows the possibility of recharging the cell for a new use [2, 3].

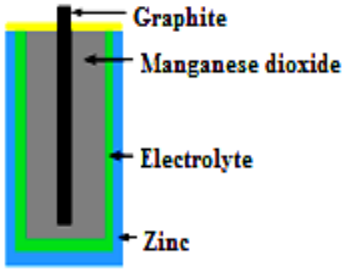

Fig. 1. Leclanché battery.

Since 1970, researchers have aimed to improve this type of battery, for example the group of J. Augustynski has studied the performance of the Zn/MnO_2 pair with a new $Mg(ClO_4)_2$-$Mg(OH)_2$ electrolyte. The main improvements made by this group compared to the traditional Leclanché cell concern hot storage and specific power [4]. Among the raw materials used in this type of battery is manganese dioxide MnO_2, it is used as a cathode. So the characteristics of the battery depend on this material. Manganese dioxide is one of the oxides that have been studied for a long time because of these crystallographic varieties, properties and applications [5].

Manganese dioxide in the form of nanoparticles may provide improvements in Leclanché-type batteries, since the physicochemical properties of the nanoparticles will be located on the border between molecular state and massive state [6]. With the reduction in size come new properties. In all cases, a significant increase in the specific surface area isobserved, that is to say a greater reactivity or accessibility to the functions, it is also possible to have new properties, which are not observed in the macroscopic material. These properties can be catalytic, magnetic, optical or others.

Schmid demonstrates that when a metallic particle, having solid metallic properties, is reduced to the size of a few dozen or even a few hundred atoms, the electron density of states in the valence and conduction bands decreases. As a result, the electronic properties are considerably modified and the separation between the bands increases as the size of the material decreases [7]. The quasi-continuous density of

electronic states is replaced by a discrete level of energy within nanoparticles.

Structurally, metal clusters exhibit a regular geometry giving rise to polyhedra (known as "magic number" clusters) (Table 2.1) [6]. They are formed by compact stack successive layers of metallic atoms around a single atom. Table 2.1 shows an idealized representation of clusters with cuboctahedral geometry. The total number of atoms, per layer, is given by the equation: **10υ2+2**. It is interesting to note that the percentage of atoms on the surface decreases as the number of atoms of a metal increases.

Clusters (Magic Number)					
Number of layers (υ)	1	2	3	4	5
Total number of atoms	13	55	147	309	561
Number of atoms in the shell (υ) = (10 υ2 + 2)	12	42	92	162	252
Percentage of surface atoms	92 %	76 %	63 %	52 %	45 %

Table 1. Representation of clusters with an octahedral cubic structure indicating the percentage of surface atoms as a function of the size of the clusters [6].

In this article we aim to synthesize MnO_2 nanoparticles in a dilute medium of ionic liquid to see the effect of ionic liquid on the sizes of NPs on the one hand and on the other hand to obtain MnO_2 nanoparticles with very small sizes.

II. SYNTHESIS OF MnO_2 NANOPARTICLES

There are many methods for synthesizing MnO_2 NPs. We have chosen a simple method; it is that of the group of Abulikemu Abulizi [8].

A dilute solution of IL and potassium permanganate was prepared, then concentrated sulfuric acid was added (dropwise) to this solution. This reaction took place under ultrasound (in an ultrasonic bath). MnO_2 crystallites were thus obtained (solid part, with a brown color), after drying a powder (NPs of MnO_2) was obtained.

III. CHARACTERIZATION BY X-RAY DIFFRACTION AND DISCUSSIONS

The sample was characterized by XRD, from which we obtained the results represented by the diagram of Fig. 2, In this diagram, we notice peaks relating to the ionic liquid and peaks characteristic of MnO_2 nanoparticles (these peaks are shown in the figure by the corresponding Miller indices).

If we compare the peaks corresponding to the MnO_2 nanoparticles in our sample with those of the diagrams in the literature, we see that they are wider. Thus, the crystallites of MnO_2 nanoparticles in our sample have smaller sizes. Calculating crystallite diameters, using Scherrer's formula (formula 1), gives sizes of the order of one nanometer.

Scherrer's formula is written as follows:

$$D = \frac{K\lambda}{\beta \cos\theta} (1)$$

Hence D is the diameter of the crystallite, λ is the monochromatic wavelength of X-rays, it has the value λ = 0,15406 nm, β is the width of the peak at half height, θ is the angle diffraction rate and K is Scherrer's constant (a form factor) which is 0,89.

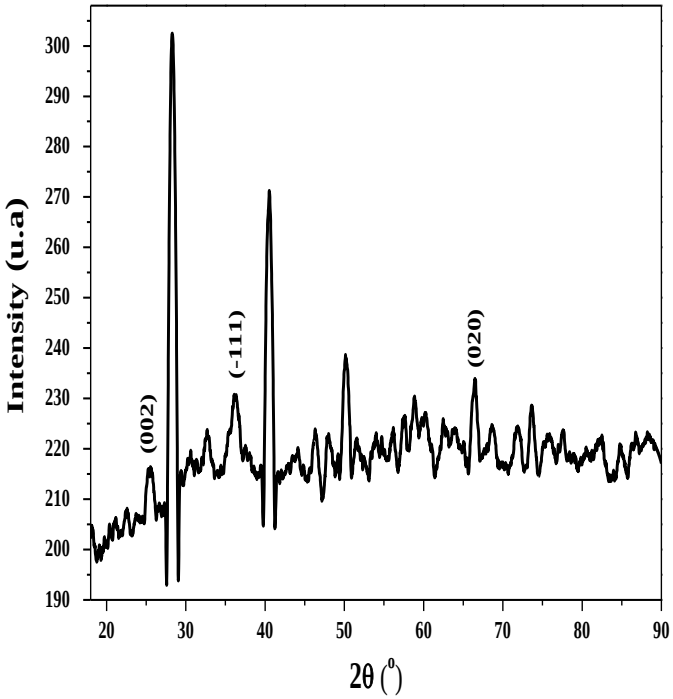

Fig. 2. DRX plot of the sample (composite of ionic liquid and MnO_2 nanoparticles).

If we use Scherrer's formula, we select the peaks positioned at the small angles, those for which the relative error on the width at half-height is small (we discard the lines located at the big angles, for which the measurement error is important), we find crystallite sizes on the order of 8 nm. So here we have NPs showing considerably reduced sizes. This implies that the MnO_2obtained in nanometric form will have new properties under the effect of two parameters; the specific surface parameter and the effect of the quantum confinementparameter. So using these MnO_2NPs as a cathode

in a battery can be very beneficial.

IV. Specific surface

From the results obtained from the DRX measurements it is clear that the specific surface area of MnO_2 nanoparticles is high.

Manganese dioxide (MnO_2) crystallizes in the tetragonal (quadratic) space group. Its structure is three-dimensional. One manganese atom bonds with six oxygen atoms to form an octahedral-shaped mixture of MnO_6 sharing edges and corners. The octahedral tilt angles, sharing the corners are 50°. There are four shorter (1,91Å) and two longer (1,93Å) Mn-O bonds. The oxygen atom is bound in a distorted trigonal plane geometry to three manganese atoms. The characteristics given according to Ferrari; a=4,380Å, c=2,856Å, c/a=0,654Å, and according to Wyckoff; a=4,44Å, c=2,89Å, c/a=0,65Å, and the unit cell volume is about 56 $Å^3$.

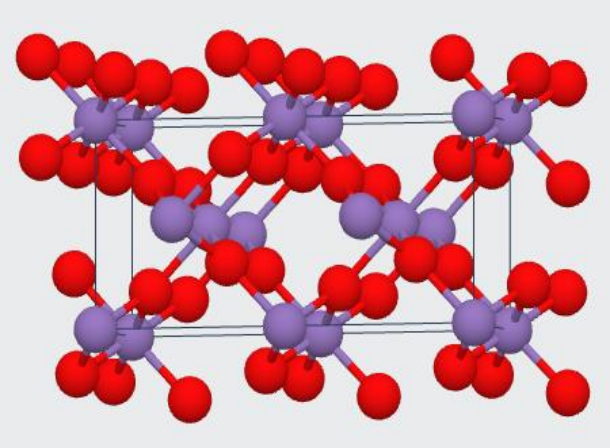

Fig. 3.Crystallographic structure of MnO_2.

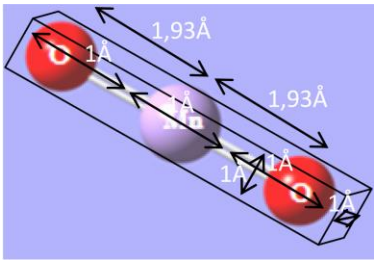

Fig. 4.the ZnO_2 molecule.

If we rely on an approach similar to that shown in Table 1, we can optimize the percentage of MnO_2 molecules on the surface of a nanoparticle. If we assume that the volume value of the nanoparticle V is of the order of D^3:

$$V = D^3 \qquad (2)$$

Therefore; $V \approx 8^3 \approx 512$ nm^3 and we know that the unit cell volume is of the order of56 $Å^3 = 5{,}6\times10^{-3}$ nm^3, we obtain a number of unit cellsper nanoparticle of the order of 9×10^4. Or in another way, if we assume that the size of the MnO_2 molecule is of the order of 4×10^{-3} nm^3 (the size of an atom is around 1Å), the number of MnO_2 molecules is found to be on the order of 13×10^5 molecules per nanoparticle. This will lead to a big number of molecules on the surface of the nanoparticle. This implies that the MnO_2 obtained in nanometric form will have a very large specific surface.

So using these MnO_2 NPs as a cathode in a battery can be very beneficial.

V. Effect of quantum confinement

Such an effect is expected in metal systems whose size is less than a few tens of nanometers. This confinement regime is characterized by a discrete electronic spectrum at very low temperature, when thermal energy is less than the energy difference between two neighboring electronic levels. This discretization of the energy spectrum implies the appearance of a gap between the energy of the ground state and that of the first excited state. Therefore, the modification of electronic properties of nanoparticles induces changes in thermodynamic properties at low temperature such as spin susceptibility. Such physical quantities are of interest because they reflect the superconducting properties [9].

VI. Conclusion

Our results show that IL has an effect on the formation of MnO_2 crystallites. Indeed, IL plays a very important role during the chemical reaction, since it stabilizes the NPs formed at reduced sizes, preventing them from agglomerating. This reduction in the size of the NPs will certainly have an influence on the properties of the MnO_2obtained; in fact the specific surfaces will be greater, which implies that the electrical properties of the material will be modified.

And the effects of quantum confinement give characteristics to the material at the border between the properties of a massive material and the properties of a microscopic material. This opens up a field of research concerning fundamental physics, that is to say the global theory which includes the three theories; Newtonian physics, relativistic physics and quantum physics.

Therefore, the use of these NPs in a pill can be very interesting and merits furtherstudy.

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