On the impact of the slurry mixing procedure in the electrochemical performance of composite electrodes for Li-ion batteries: A case study for mesocarbon microbeads (MCMB) graphite and Co_3O_4

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ABSTRACT

The influence of the slurry mixing procedure on the homogeneity and electrochemical performance of composite electrodes for Li-ion batteries was studied. MCMB graphite and Co_3O_4 were used as probe active materials, since they exhibit different reaction mechanisms with lithium. Three different mixing procedures were used, (i) magnetic stirring, (ii) magnetic stirring with additional sonication steps and (iii) ball milling. SEM studies allow to determine that the mixing procedure has a significant effect in the microstructure of the active material. Indeed, ball milling was found to destroy the pristine MCMB microstructure and to induce agglomeration in nanosized Co_3O_4. While magnetic stirring is much less aggressive to that respect, sonication steps were found to enhance the homogeneity of the mixture without inducing major modifications in the microstructure of the materials and hence to have a beneficial impact in the final electrochemical performance.

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1. Introduction

Developments in materials chemistry have been crucial in the ever increasing performance of lithium ion batteries [1] owing to both the discovery of brand new phases and the tailored modification of already known ones (doping, changes in particle size and shape, defects, carbon coating, etc.). Indeed, electrode materials and their intrinsic properties (e.g. ionic and electronic conductivity) determine battery voltage and energy density and hence govern battery expected performance. Even if industrial research has always considered the importance of the electrode fabrication processes in the final performance, this factor has unfortunately often been disregarded in academic fundamental research. Nonetheless, some papers published during the last decade clearly proved that formulation is a key factor in terms of electrochemical performances of composite electrodes for Li-Ion batteries [2–4]. Among the several parameters already identified as strongly influencing the performance of a composite electrode we can mention: (i) the composition of the slurry from which the composite electrode is fabricated (relative amounts of active material (AM) and

additives) [2], (ii) the nature of such additives (mostly binder (B) and carbon additives (Cadd) but also surfactant (S)) [3,5,6] and (iii) the porosity of the composite electrode [7]. Careful optimisation of these parameters can greatly improve the electrochemical behaviour in terms of practically achieved specific capacity, capacity retention upon cycling as well as tolerance to high cycling rates.

Among the different factors influencing the behaviour of a composite electrode, the homogeneity in the mixing of the various components is certainly one of the most important. Indeed, since most of the AMs used in batteries are poor electronic conductors, a highly intimate mixing with the Cadd is required in order to increase the AM/Cadd contact point interface, thus allowing a more homogeneous current density throughout the electrode [8]. An interesting approach to improve the homogeneity is the use of surfactants to increase the degree of dispersion in the slurry [6,9]. Furthermore, Guy et al. have demonstrated that a preliminary sonication step for the Cadd in the presence of a plasticizer greatly improve the dispersion, and hence the electrochemical performance of the composite electrode [10].

While most of the time the slurry mixing procedure is not mentioned in the scientific literature, two different methodologies are generally used in studies dealing with electrode materials research: hand-mixing in a mortar and ball milling. A recent interesting example highlighting the importance of the mixing procedure deals with, "soft" mixing by magnetic stirring of precipitated Co_3O_4 in

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order to preserve pristine material porosity as a way to improve the capacity retention upon cycling [11].

Basing on studies showing that ultrasonic irradiation is much more efficient than ball milling for achieving highly dispersed suspension of nanoparticles [12] we decided to undertake a study on the influence of the slurry mixing procedures in the final electrochemical performances of the resulting composite electrodes. Three methods have been compared (i) magnetic stirring, (ii) magnetic stirring + ultrasonic irradiation and (iii) ball milling. Both well known MCMB 25-28 graphite and commercially available nanosized Co_3O_4 have been chosen in the present study as probe materials. While graphite is in use as negative electrode material in commercial batteries and reacts with lithium through a conventional insertion process, Co_3O_4 is still far from application. It operates through a conversion reaction mechanism [13] yielding cobalt metal nanoparticles embedded in a Li_2O matrix upon reduction. Even if this entails capacities much higher than those of graphite, the large hysteresis between charge and discharge is still a key issue to overcome for commercial application. Studies dealing with electrode formulation optimisation for conversion materials are scarce and mostly limited to the impact of the binder choice [4] or the percent of Cadd [14]. The reported improvements indicate that this research topic is well worth pursuing.

2. Experimental

MCMB 25-28 (Osaka Gas Co.) was used as received while nanosized Co_3O_4 (Aldrich) was previously annealed at 400 °C for 6 h under air to achieve its nominal oxygen content (as confirmed by TGA experiments). Further annealing was performed at 800 °C for 6 h in air in order to increase particle size. For sake of conciseness, these samples are respectively referred to CO4 and CO8, respectively, throughout this article.

In all cases slurries were prepared by mixing 84 wt.% of AM (e.g. Co_3O_4 or MCMB), 8 wt.% of Polyvinylidene fluoride (PVDF, Arkema) as a binder and 8 wt.% of Super P carbon (Csp hereafter from Timcal) in N-Methylpyrrolidone (NMP, Aldrich). Mixing of the slurries was performed under air following three different protocols; (i) magnetic stirring for 15 h (denoted -NS), (ii) magnetic stirring for 15 h, the vial containing the slurry being placed in an ultrasonic bath for 10 min every 5 h (denoted -S) and (iii) ball milling in a stainless steel container with 3 stainless steel balls of 1 cm diameter at 500 rpm for 1 h with change of the rotating way every 30 min using a PM100 Retsch planetary Ball Mill (denoted -M). Composite electrodes were prepared by tape casting of each slurry on a 20 μm thick copper foil (Goodfellow) with a 250 μm Doctor-Blade and further dried at 120 °C under vacuum. Once dried, 0.8 cm² disk electrodes were cut, pressed at 6 t and tested in Swagelok type cells with a disk of Li metal foil (Chemetall) as counter and reference electrode. Two sheets of Whattman GF/d borosilicate glass fiber were used as a separator, soaked with the electrolyte (ca. 0.5 cm³ of 1 M LiPF6 in EC:DMC 1:1 (LP30, Merck)). Electrochemical cycling experiments were made in galvanostatic mode with potential limitation (GCPL) using either an Arbin BT2042 or a Bio-Logic VMP3 potentiostat. Reproducibility was checked by assembly of twin cells. A systematic cycling procedure was used in all cases. Successions of 10 cycles at different C rates were applied to check the electrochemical behaviour at these rates and determine whether high rates were detrimental to the electrode performance. First, 10 cycles were performed at C/5 followed by 10 cycles at C, C/5, 2C and finally C/5.

Scanning Electron Microscopy (SEM) studies were performed using a Quanta 200 ESEM FEG FEI microscope.

X-ray powder diffraction (XRD) was performed on a Siemens D5000 diffractometer with Cu Kα radiation (1.5418 Å).

3. Results and discussion

3.1. XRD and SEM study

Fig. 1 shows the X-ray diffraction patterns of the pristine MCMB (Fig. 1a) and Co_3O_4 (Fig. 1b) powders, confirming their purity. These samples were also examined by SEM and the effect of the mixing conditions was ascertained. Typical micrographs of the pristine material can be seen in Fig. 2a, d and g (respectively for MCMB, CO4 and CO8). Fig. 2b, e and h shows the same pristine powders after treatment in the same mixing conditions than the slurries but without addition of PVDF and Csp (magnetic stirring + sonication procedure in cyclohexane and drying at room temperature overnight). Finally, Fig. 2c, f and i depicts typical micrographs for the AMs (MCMB, CO4 and CO8) after a ball milling procedure without any additive.

We can see from the SEM micrographs of the pristine MCMB (cf. Fig. 2a), and MCMB after magnetic stirring + sonication (cf. Fig. 2b) and ball milling (cf. Fig. 2c) that there is a significant influence of the mixing procedure in the microstructural features. Indeed, in the case of the pristine powder and the sample subjected to magnetic stirring + sonication the initial "ball like" morphology is preserved. When ball milling was applied, the initial microstructure is transformed and "plate like" particles are obtained. The microstructure of graphite has been pointed out to be of tremendous importance in terms of electrochemical performances [15–17]. Thus, one would expect the changes induced by ball milling to be detrimental for the electrochemical performance of MCMB, as will be further discussed in the next section. It is also worth mentioning that a sonication procedure allows us to achieve smaller "MCMB balls" as compared to the pristine powder (cf. Fig. 2a and b). Indeed, while particle diameters in the latter range from 25 to 50 μm, 7–35 μm particles are obtained after magnetic stirring with sonication steps, the ball like morphology being preserved. After a prolonged sonication procedure (5 h of irradiation) particles larger than 27 μm are no longer observable.

The pristine CO4 powder is composed of micron-size agglomerates with secondary particles with a mean diameter of ca. 38 nm ± 5 nm (cf. Fig. 2b). After a mixing procedure including sonication steps, agglomerates are no longer observable and the powder is thus constituted of isolated nanoparticles with a mean diameter around 35 nm ± 5 nm (cf. Fig. 2e). When ball milling is applied larger particles with larger size distribution (ca. 60 nm ± 20 nm) are obtained (cf. Fig. 2f) as a result of agglomeration. As expected, much larger particle sizes are obtained for CO8 (larger than ca. 700 nm) compared to CO4, no matter the mixing procedure.

Fig. 3 shows typical micrographs of all the composite electrodes prior to testing. They are taken in backscattering mode, in which the contrast is mainly due to the difference in molecular weight of the imaged particles. The electrode being pressed, the topographical component of the contrast is very low. In the case of electrodes prepared with MCMB, since the AM is a carbonaceous type material it is impossible to dissociate the area of AM from areas with binder and Cadd from back scattering SEM micrographs. The differences in homogeneity are hence much better determined for electrodes prepared with CO4 and CO8 samples for which bright spots are ascribable to Co_3O_4 and dark spots to the carbon additive and binder. Comparison of Fig. 3d and e allows determining the influence of sonication for nanosized CO4. While bright and dark spots are clearly identified in the first, the composite electrodes in Fig. 3e, prepared via sonication mixing, present very uniform composition with much smaller bright areas. It is also worth mentioning that comparison between Fig. 3e and f indicates a more homogeneous mixing of the AM (CO4) and the additives with a sonication procedure (smaller bright spots). Sonication steps result thus in major improvement of the composite electrode homogeneity. In
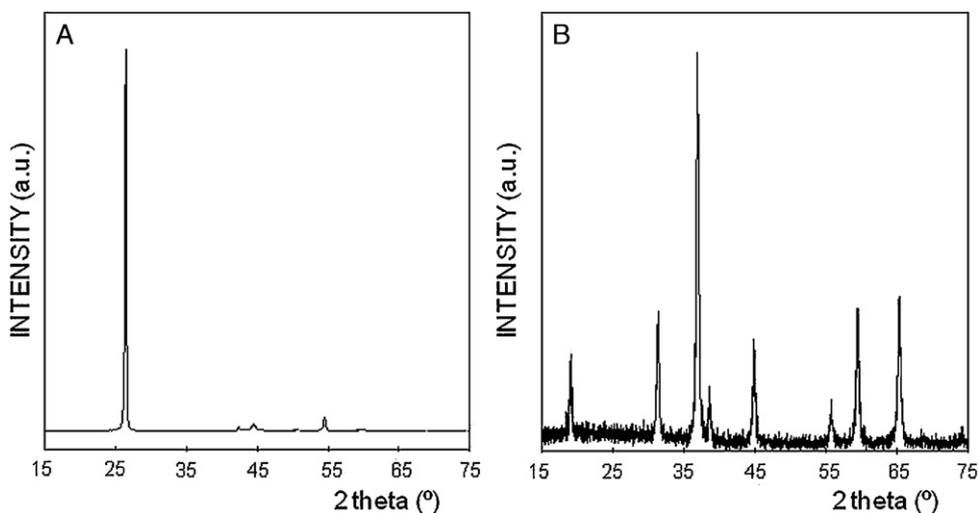
Fig. 1. X-Ray diffraction diagrams of the pristine (a) MCMB, (b) Co_3O_4.

the case of CO8, slightly better homogeneity of the composite electrodes is achieved by sonication procedures compared to mixing via magnetic stirring and by ball milling (cf. Fig. 3g, h and i).

In summary, the SEM study allows to conclude that the mixing procedure is of tremendous importance in terms of the final morphology of the pristine powder and strongly influences the homogeneity of the composite electrode. In the case of MCMB, while ball milling completely destroys the initial structure of the material, "soft" mixing (i.e. magnetic stirring and sonication) allow maintaining the "ball like" morphology of the pristine powder (not visible on the SEM micrographs of the composite electrode). Furthermore, sonication allows a significant decrease of the size of the MCMB particles. For CO4, well dispersed secondary particles (breaking of the agglomerates) can be achieved either by sonication or ball milling. While the former allows conservation of the initial secondary particle size, the latter induces some agglomeration.

3.2. Electrochemical testing

To determine the influence of the slurry mixing procedure and the induced microstructural changes on the electrochemical performance of the electrodes prepared, GCPLs were carried out at different C rates (ca. C/5, C and 2C). Most relevant results are shown in Figs. 4 and 5.

Fig. 4a shows the voltage versus capacity profiles for MCMB electrodes which exhibit the classical electrochemical behaviour for graphitized materials regardless of the mixing procedure [15]. IR drops have been measured at the end of the first reduction and first reoxidation and found to be similar within experimental error (ca. 25 mV). However, the plot of the capacity versus cycle number (cf. Fig. 5a) clearly demonstrates an important effect of the mixing method on the capacity values achieved. Indeed, in all cases after a slight decrease in capacity on the first cycle due to the SEI formation, capacity at C/5 reaches stable values: ca. 270 mAh g^{-1} for the magnetically stirred MCMB, and ca. 310 mAh g^{-1} for the ball milled while a capacity as high as 380 mAh g^{-1} is obtained for MCMB electrodes prepared with the procedure including sonication steps. The theoretical capacity of graphite being 372 mAh g^{-1}, these results demonstrate the effectiveness of the sonication steps in the mixing procedure. Furthermore, the coulombic efficiency on the first cycle is also the highest in the case of the sonicated slurry with 79% as compared to 75% for the one prepared by magnetic stirring and 71% in the case of the ball milled. Coulombic efficiencies in all cases reach ca. 99% after the first cycle. More interestingly, the capacity retention at higher C rate is also improved for the

electrodes prepared from sonication (cf. inset of Fig. 4a). Indeed, while electrodes prepared by ball milling or magnetic stirring only retained about 40% and 20% of the C/5 capacity at C and 2C, those prepared by sonication retained more than 70% and 30% of the C/5 capacity at C and 2C. These results are in agreement with major microstructural changes on the MCMB being induced by ball milling or magnetic stirring mixing procedures (cf. Fig. 2a and c). Alternatively the mixing procedure including sonication steps induces a certain reduction of the MCMB particle sizes (cf. Fig. 2b), and hence increases the AM/electrolyte interface (which would explain the higher specific capacity achieved at a certain rate) and shortens the Li diffusion pathway (and hence promotes higher performance at high C rate).

It is worth mentioning, that literature reports for MCMB performance are varied. Indeed, specific capacities ranging from 200 mAh g^{-1} up to 350 mAh g^{-1} have been reported at C/5 or lower C rates [18,19], and specific capacities ranging from 36 mAh g^{-1} up to 330 mAh g^{-1} have been reported at C [20,21]. Although the mixing procedure and the MCMB type (2328; 2528; etc.) are not always mentioned in the literature, our work clearly demonstrates that the mixing procedure of the slurry can strongly modify the MCMB microstructure and hence has an important influence in the electrochemical performances. In the present study capacities higher than 370, 250 and 100 mAh g^{-1} at C/5, C and 2C, are reported which compare very well with the actual current literature standards. Furthermore, since no specific attention has been paid in this work to the formulation of the composite electrode (amount and type of binder and conducting additive) we may expect that the performances at high C rates could be further improved.

Fig. 4b and c displays the voltage versus capacity profile obtained by GCPL CO4 and CO8 electrodes prepared with the three different mixing procedures, exhibiting typical behaviour for conversion reaction electrode materials [13] and most specifically Co_3O_4. Indeed, the first reduction exhibits three components (i) a first plateau at ca. 1.25 V versus Li$^+$/Li (noted α) which is only observable for CO4 and has been associated with a lithium insertion process and formation of a Li–Co–O intermediate phase and observed only for low current density (small C rate and/or small particles) [22], (ii) a second plateau at ca. 1.15 V versus Li$^+$/Li (noted β) which would be related to the conversion process itself to yield Co nanoparticles embedded in a Li$_2$O matrix and (iii) an almost linear potential decay below 1.15 V versus Li$^+$/Li (noted γ) typically observed in conversion reaction materials for which two alternative origins (electrolyte decomposition and interfacial storage [13,pE184]) have been proposed. Upon reoxidation, a large volt-
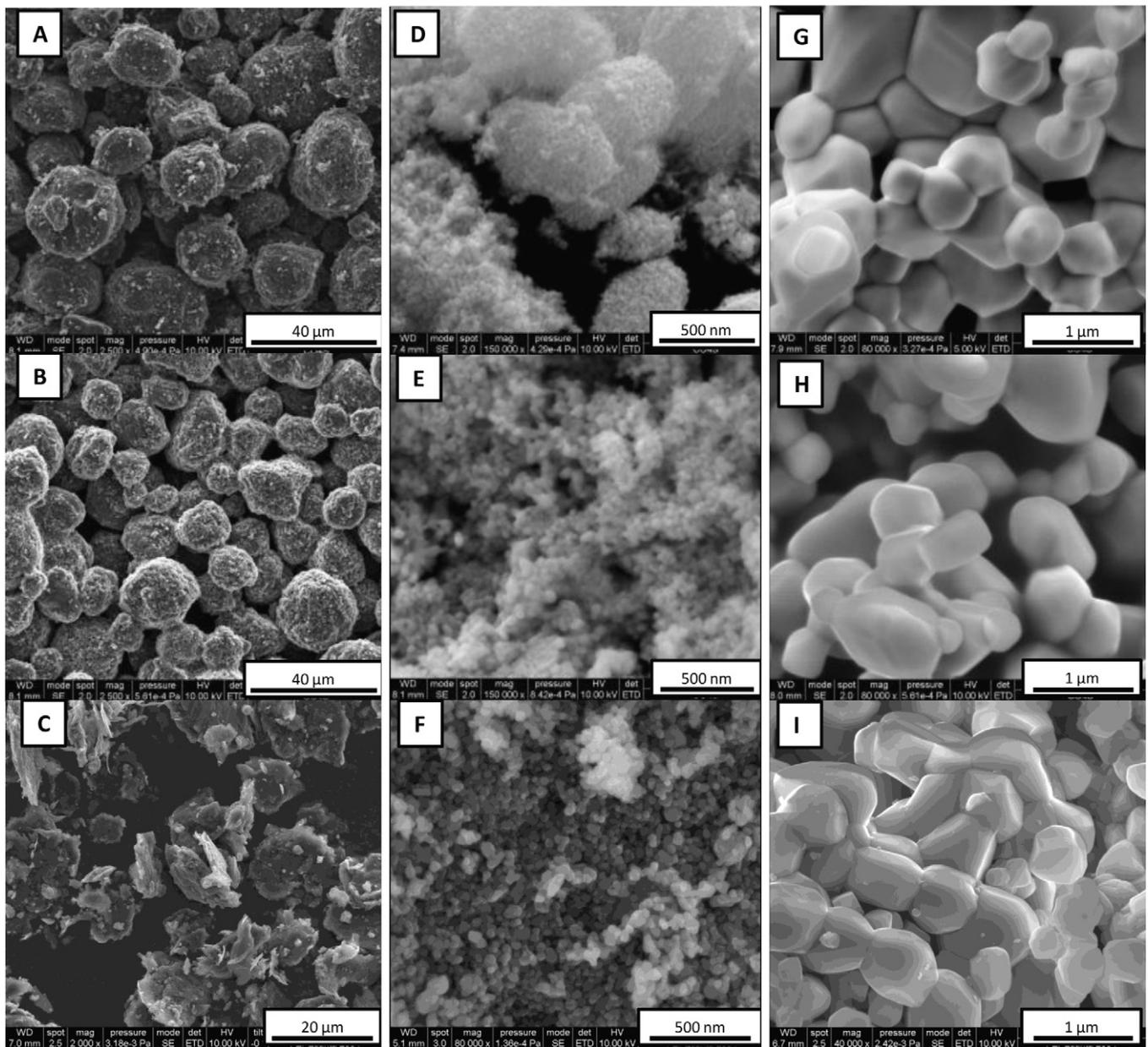
Fig. 2. SEM micrographs of powder of MCMB (a, b and c); CO4 (d, e and f) and CO8 (g, h and i). The powders were previously: magnetically stirred in Cyclohexane (a, d and g); magnetically stirred and sonicated in cyclohexane (b, e and h) or ball milled without any additive (c, f and i).

age hysteresis is observed together with an important coulombic inefficiency, also typical features for conversion reaction materials. The γ component in the total first discharge capacity is roughly the same for each sample, being independent of the slurry mixing procedure: ca. 35% in the case of CO4 and much lower (ca. 28%) for CO8. Thus, while homogeneity in active material distribution does not affect the phenomenon, its particle size has an important effect. This would be in agreement with electrolyte decomposition at low voltages being enhanced/catalyzed for lower particle sizes in the transition metal oxides, which seems a reasonable assumption. Finally, it is interesting to note that slightly higher voltage hysteresis is observed for Co_3O_4 nanoparticles (ca. 0.85 V) as compared to ca. 0.74 V for micron size Co_3O_4. This increase of polarisation for smaller particles has also been reported previously by Larcher et al. [22]. These large values are in agreement with this phenomenon being intrinsic to the conversion reaction mechanism [23,24] and not rooted on low conductivity. Indeed, first cycle IR drops have been measured and found to range from 10 to 15 mV, in agree-

ment with the values observed for MCMB electrodes and also with reports on low electrode resistivities for carbon additive content higher than 5% [25].

Capacity versus cycle number for CO8 electrodes prepared from slurries mixed either by magnetic stirring, sonication or ball milling, and the results are displayed in Figs. 4c and 5c. The capacity values achieved are again strongly influenced by the slurry mixing method (cf. Fig. 5c) while the general trend in capacity retention is the same for all mixing procedures. An important decrease in the capacity is observed during the first three cycles to reach a constant value which is found to depend on the slurry mixing method and the C rate. For instance, a reversible capacity of 500 mAh g^{-1} is achieved at C/5 for the sonicated CO8, whereas only 300 mAh g^{-1} is obtained at the same C rate when using the magnetic stirring and the ball milling procedures. The higher capacity values for the electrodes prepared from slurries mixed with sonication step are certainly due to better homogeneity in the mixture (cf. Fig. 2g, h and i), thus allowing higher active material utilization.
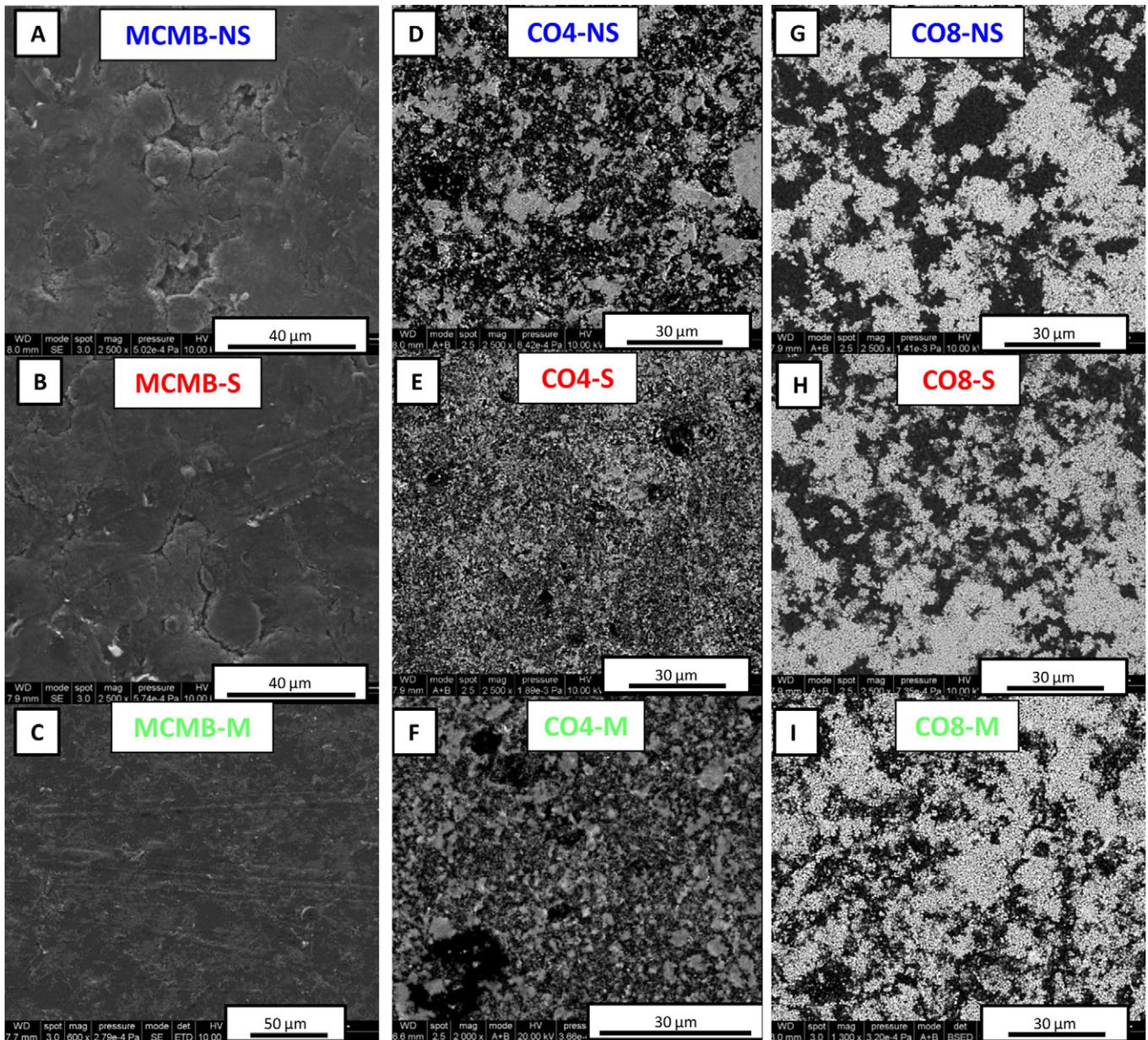
Fig. 3. SEM micrographs of composite electrodes (84% of AM, 8% of Csp and 8% of PVDF) with AM being: MCMB (a, b and c); CO4 (d, e and f) and CO8 (g, h and i). The slurries were previously: magnetically stirred (denoted -NS; a, d and g); magnetically stirred and sonicated (denoted -S; b, e and h) or ball milled (denoted -M; c, f and i).
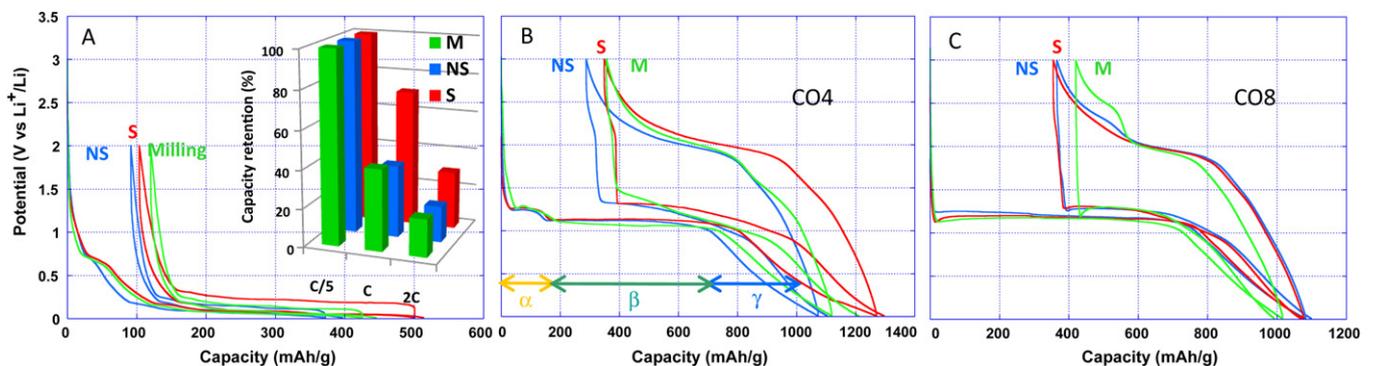

Fig. 4. Voltage versus capacity profiles of composite electrodes displayed in Fig. 3 (first cycle recorded at C/5). The AM being: (a) MCMB, (b) CO4 and (c) CO8. Inset in (a) presents the capacity retention of MCMB electrodes cycled at C and 2C expressed in percents with respect to capacities recorded at C/5.
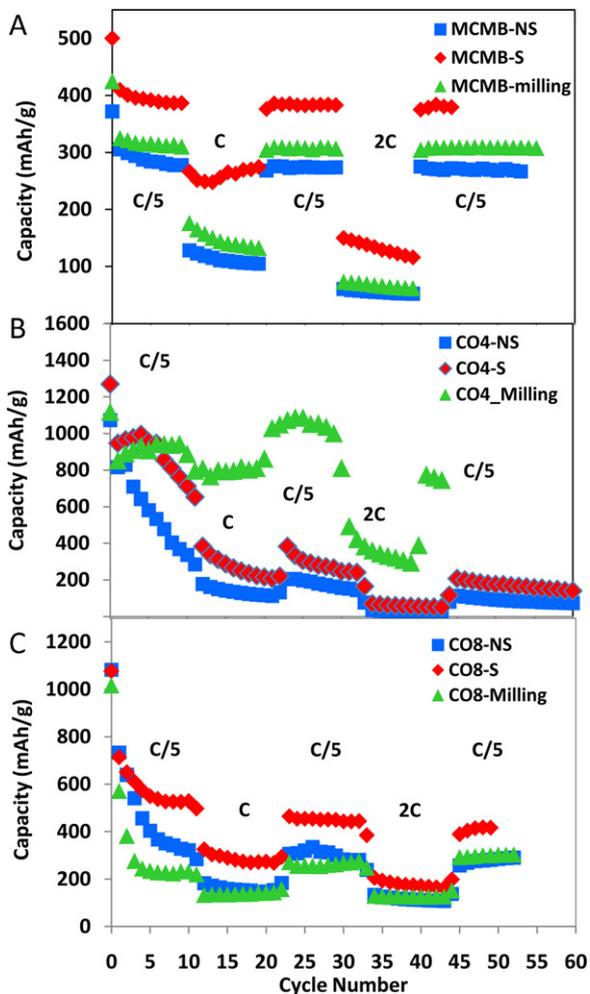
Fig. 5. Discharge capacities versus number of cycles of composite electrodes displayed in Fig. 3. The AM being: (a) MCMB, (b) CO4 and (c) CO8.

Fig. 5b displays the discharge capacities versus the number of cycles for the CO4 prepared with the three different mixing procedures. In contrast to the above mentioned results, the capacity retention for CO4 is found to be strongly correlated to the slurry mixing procedure. Even if sonication steps are beneficial in terms of capacity as observed for MCMB and CO8, both electrodes prepared from slurries mixed through simple magnetic stirring or magnetic stirring with sonication steps exhibit severe capacity losses upon cycling, as widely reported for nanosized conversion reaction materials [22,26], and discussed below. Interestingly, even if the electrode prepared via ball milling shows lower discharge capacities during the first six cycles compared to electrode prepared by sonication (in agreement with the better homogeneity observed by SEM for sonicated slurry, cf. Fig. 3e and f), it exhibits much better capacity retention. This is attributed to the different Co_3O_4 particle sizes (ca. 35 nm ± 5 nm for sonication versus 60 nm ± 20 nm for ball milling). The possible causes for the higher capacity fade observed with small particles have already been discussed in several previous studies. Mainly two hypothesis have been suggested: (i) enhanced electrolyte degradation due to a larger material/electrolyte interface, leading to electrical contact loss by formation of a poor electrical conductive gel like film [27], (ii) dissolution of the cobalt in the electrolyte, further enhanced for highly dispersed powder [11]. Larcher et al. demonstrated that capacity fading is strongly enhanced for crystallite sizes below 47 nm (BET surface area higher than $10\,m^2\,g^{-1}$) [22], in agreement with results from Kang et al. [28]. A more systematic study of the influence of the

particle size and of the formulation of the electrodes is underway to address this point.

4. Conclusion

In this work three different slurry mixing procedures (magnetic stirring, magnetic stirring + sonication and ball milling) have been applied to electrode preparation using both Co_3O_4 with different particle sizes (CO4, CO8) and MCMB graphite as active materials. The slurry mixing procedure is found to affect the microstructure of the pristine active material as well as the homogeneity of the composite electrode, thus inducing differences in the electrochemical performances. Ball milling (the most common way to prepare slurries), induce the destruction of the ball like structure of MCMB, and thus decreasing the capacity values achieved. In contrast, the magnetic stirring with sonication steps preserve the structure of MCMB while ensuring mixture homogeneity resulting in electrochemical performances among the best reported for the time being for commercial MCMB. Similar trends are observed for Co_3O_4 micron size particles, for which magnetic stirring with sonication steps results in the best electrochemical performance. In the case of CO4 (micron size agglomerates of 35 nm particles) both ball milling and magnetic stirring with sonication procedures induce a dispersion of the secondary particles from the agglomerates. In the case of the sonicated slurry the secondary particles preserve similar sizes as those of the pristine powder, while larger particles are obtained in the case of ball milling, which is certainly the cause of the higher capacity retention exhibited by this sample, in agreement with literature reports suggesting a critical Co_3O_4 particle size value for good cyclability.

In summary, though discussion on the slurry mixing procedure is seldom present in the literature when reporting electrochemical performance of materials, our results prove that it is well worth taking into consideration. Indeed, ball milling, which is the simplest and most widely used method at the laboratory scale, can significantly modify pristine active material microstructure and hence be detrimental to their electrochemical performances. In contrast, sonication steps are found to be an effective "soft" way of destroying particle agglomerates and increasing the mixture homogeneity while preserving the pristine material microstructure.

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