

Nanoporous Ag-CNTs foamed electrode for lithium intercalation

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Abstract

Intercalation of lithium into Ag-CNTs sample is reported here. We have used a nano-porous silver foam as a frame for deposition of the CNTs inside the pores by electrophoresis deposition (EPD) technique. By using chronopotentiometry method, we have noticed that the Li storage capacity of the prepared Ag-CNTs electrode was improved noticeably in comparison with literature. In addition, a very good functional stability for the prepared electrode has been tested during subsequent cycles of charge / discharge (C&D) procedures. By scanning the cycle's regulated current from 0.2 up to 1.0 mA, it was shown that in the range of 0.4–0.6 mA reversibility of the C&D capacity became optimum and the voltage profiles were converged, as well.

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1. Introduction

Li-ion batteries have been widely used in portable electronic devices due to their high energy density, high operating voltage and excellent charge and discharge (C&D) cyclic stability [1–3]. For these applications, it is critical that Li-ion batteries should have high capacity

and good rate performance [3]. Carbon materials [3–5], such as CNTs have been widely used as conductive additives in fabrication of the battery's working electrode because of their high electrical conductivity. To effectively utilize the active materials in the electrode, the contents of these

CNT additives should be often reach up to 10~20 wt.%.

On the other hand, some unexpected new symptoms such as electrochemical agglomeration, unstable SEI film formation [6] and so on, lead to significant capacity fading due to deteriorated electric contact between particles. Therefore, it would be the most promising approach to make improvement in dispersing carbonaceous particles well on some substrate materials in order to attain better cycling stability [7].

Here we report our efforts to fabricate higher performance working electrodes in electrochemical applications from mechanical and electrical point of view. An effective strategy that pins the CNTs into the nano-scale pores of the silver foam substrate by using electrophoresis deposition (EPD) technique [8]. The defused CNTs inside pores of the silver foam made better inter-junctions with it, therefore; the charge exchange process on the surface of the electrode has been facilitated in electrochemical usages. In spite of higher weight percentage of the CNTs content, such a structure of the porous silver electrode is beneficial to buffer the volume variation of the CNTs during lithium adsorption (charging) and desorption (discharging) periods [9].

Finally, we have tried to optimize the lithium storage capacity in the working electrode by scanning the applied cyclic current in the chronopotentiometry measurements and the optimum Li storage capacity was achieved in the range of 0.4–0.6 mA of the current.

2 Experimental

2.1 Electrode preparation

The used CNTs in this study have been synthesized by CVD method with Mo

catalyst and they were purified by acidic and thermal treatments [10]. XRD, TEM and TGA results show high purity level of the prepared sample, Fig. 1. Some scarce catalyst nanoparticles are always observed (attached to the CNTs) in the TEM images, even after the purification process, but the sharp slope of the TGA curve indicates that the sample is comprised mostly by CNTs with burning temperature around 550 °C [11].

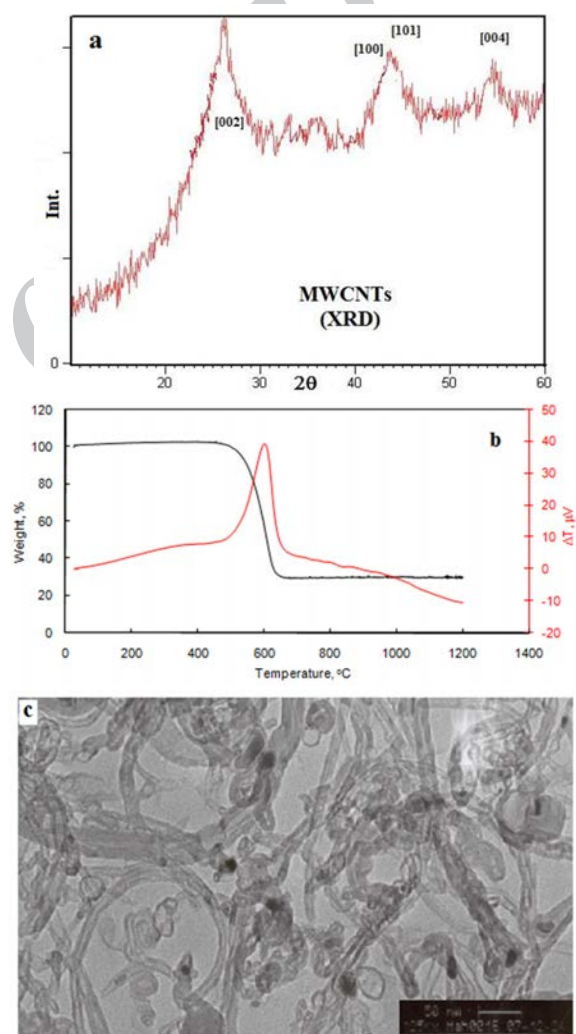


Fig. 1. (a) XRD pattern of the MWCNTs with indicative characteristics reflections, (b) TGA graph shows that the majority of the CNTs burn around 550 °C, (c) TEM image of the sample with some trace of the catalysts.

On the other hand, a nano-scaled porous silver foam has been used as the frame part of the prepared electrodes (though the foam fabrication details will be presented elsewhere), Fig.2. Using $2 \times 1 \text{ cm}^2$ pieces of the foam for nesting the CNTs inside its nano-scale pores by EPD method cause that the prepared Ag-CNTs electrodes contain so many interconnections between the CNT particles and the silver frame. This structure of the electrodes not only facilitates charge exchange inside them, but also causes a reasonable functional stability (without using any glue or binder for holding the CNTs). In order to perform the EPD process, we have hanged each of the foam plates in a dilute suspension of pantheon and the CNTs under 80 volts potential difference between the plate and a Pt electrode (15 minutes) [8]. To avoid agglomeration of the CNTs in the suspension the whole package has put inside a low frequency vibrating bath as well.

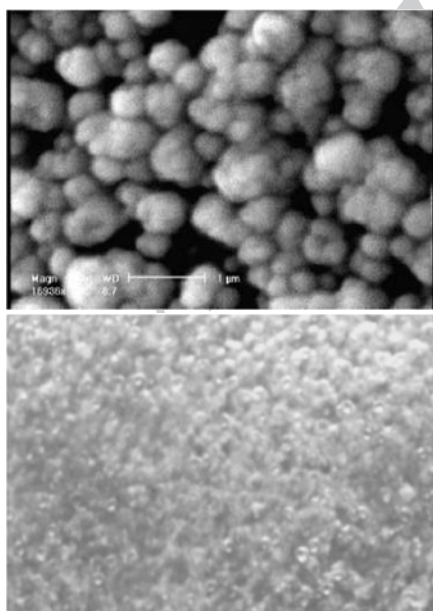


Fig. 2. (Up) TEM image of the Ag foam surface with nano-scale porosity, (Down) magnified normal image of the foam surface.

2.2 Electrochemical system

Chronopotentiometry technique with a three-electrode cell has been employed in the electrochemical study. Ag-CNTs, Ag/AgCl and Pt electrodes have been used as the working, reference and counter electrodes in the cell. The cell electrolyte was 1M LiClO_4 in a mixture of 50% ethylene carbonate (EC) and 50% diethyl carbonate (DEC) by volume. The C&D cycles were set between 0 to 3.0 voltage limits and the cell's regulated current were scanned from 0.2 up to 1 mA. Lithium ions were intercalated into the CNTs during charging half and released during discharging half of the cycles. In comparison with the bare Ag foam electrode, measuring a noticeable higher discharge capacity for the prepared Ag-CNTs electrodes indicates that the used CNTs are capable to adsorb a considerable amount of lithium ions. By the way, during many successive C&D cycles, a considerable disintegration of the CNTs from the silver foam has not been seen.

3 Voltage profiles and discussion

3.1 Ag foamed electrode

Charge and discharge profiles of a plane silver plate and the bare Ag foam (without loaded the CNTs) have been measured firstly and the results are shown in Fig. 3. In spite of a very low storage capacity in comparison with the Ag-CNTs electrodes measurements, the foamed sample exhibits several times higher capacity than the plane electrode of silver. This seems to be a new finding in comparison with Wu et al. report [9] and definitely can be attributed to quality of the foam and its huge specific surface area.

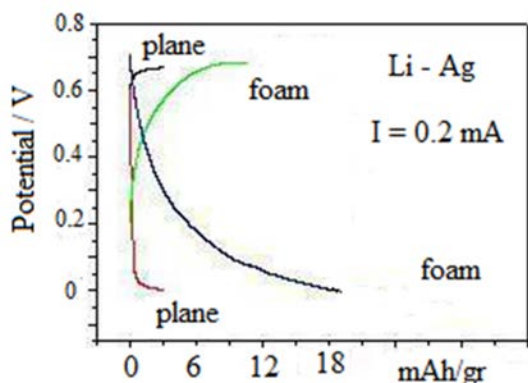


Fig. 3. Comparison between plane and the foamed silver during Charge and Discharge voltage profile.

Normally, intercalation of Li ions causes a significant volume expansion of the host structure [12], and this volume changes during a long time C&D cyclic usages leads to fading of mechanical stability of the working electrode. In this study, using the porous structure of the foam has suppressed this deficiency and all prepared electrodes have shown very notable functional stability during successive cycles and also the scanning procedure of the regulated current.

On the other hand, assuming that insertion sites are not distributed uniformly inside the Ag foam due to intrinsic lattice defects, Li ions may be inserted at some electrochemically active sites and consequently, the adsorption is influenced by the distribution of the active sites for charge transfer in the Ag foam, as well [12].

3.2 Ag-CNTs electrode

Fig.4 shows the typical voltage profiles of first, sixth and eleventh charge and discharge cycles for the Ag-CNTs electrode according to the regulated currents as : $I = 0.2, 0.4, 0.6, 0.8$ and 1 mA. In the case of $I = 0.2$ mA upon

the first discharge process the cell voltage initially drops rapidly until it reaches about 0.8 V where there is a plateau for a considerable amount of time. The plateau has been reported for the influence of amorphous forms of carbon previously [13, 14] and this removes gradually during subsequent cycles, probably because the interconnections between the silver frame and the CNTs have been stabilized after several times of lithiating and delithiating and consequently, the effect of non-conducting carbons could be short cut. In the 1st discharge the profile went below 0.3 V after a sharp decline from 0.8 V and for the subsequent cycles the major part of the discharge profile remains below 0.3 V. During next cycles, lithium intercalation occurs as the cell voltages increase until they reach about 1.0 V with same slope (but very little adsorption capacity) and then they start to increase gradually with different slopes toward the cutoff limit of 3.0 V (main part of storage occurs). A similar behavior generally can be seen also for the discharge profiles, e.g. a sharp voltage drop (from 3.0 to 2.0 V) with same slope and gradually decreasing to below 0.5 V with different slopes. In battery's terminology, "reversible capacity ratio" (RCR) defines as the ratio of capacity displayed in the charging half to total discharge capacity and here, during the first cycle it was about 0.40 and for subsequent cycles reached to about 0.50 . This increasing of the RCR can be attributed to re-arrangement procedure of the CNTs inside the pores of the Ag foam during the next C&D cycles.

By scanning the regulated current, with steps of 0.2 mA, up to 1 mA and running 11

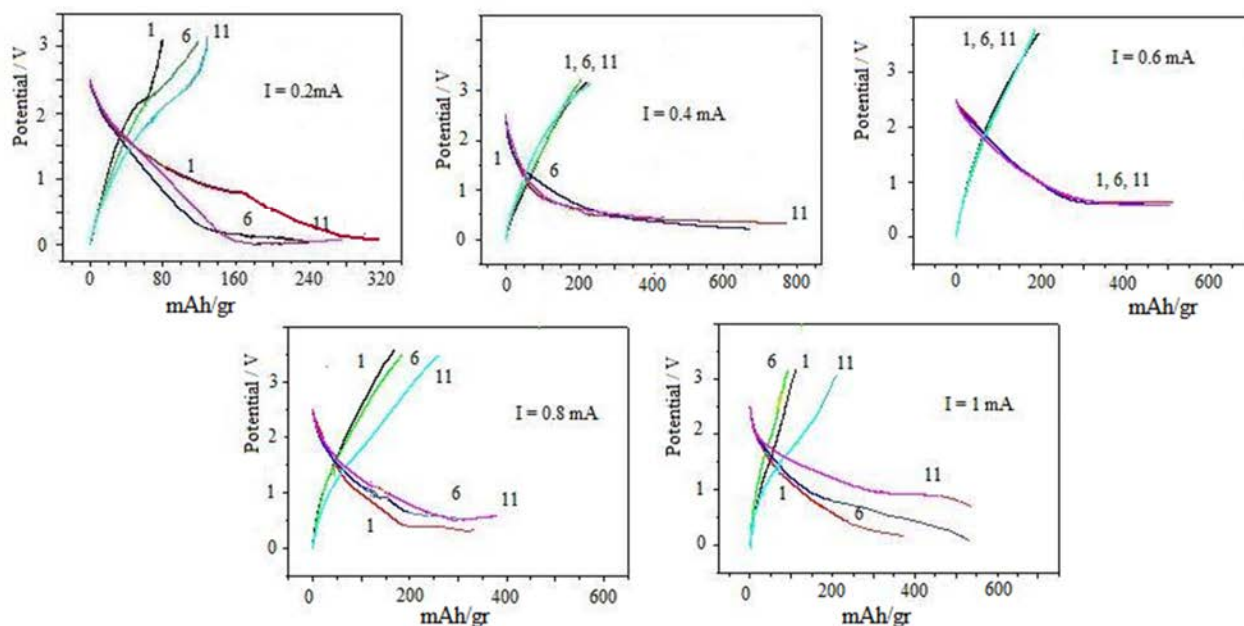


Fig.4. Regulated current C&D voltage profile scans for: $I = 0.2, 0.4, 0.6, 0.8$ and 1.0 mA. Numbers on the graphs show the corresponding cycle numbers

cycles in each step (see Fig. 4), it can be seen that the discharge profiles behave in the aforementioned general trend. However, a noticeable point occurs in the range of; $I = 0.4-0.6$ mA, because the cycle profiles were converged and coincidental and also the reversible discharge capacity became optimized at $I = 0.4$ mA.

For higher amount of scanning currents the profiles according to the different cycles were diverged along with reduction in the reversible capacity. Here, probably the electrolyte decomposition and therefore, formation of a SEI film on the surface of CNTs plays a major role.

Because the rate of electrolyte decomposition and the SEI film formation depend on charge exchange rate near the surface of the working electrode with certainty, therefore the divergence of voltage profiles by increasing

the regulated current value seems to be rational.

Fig. 5 shows XRD pattern of the working electrode after a cyclic application and the presence of extra lines in the pattern indicates formation of the SEI film on its surface [6].

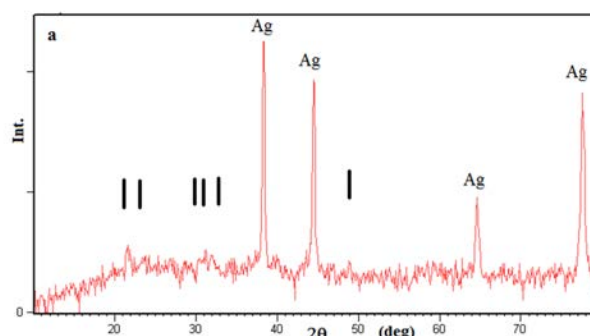


Fig. 5. XRD pattern of the Ag-CNTs electrode after some C&D cyclic Li storage and marked peaks belong to Li_2CO_3 precipitate. This is an indicative for formation of the SEI film [6]

4. Conclusion

Improvement of functional performance of CNTs contains electrodes for electrochemical lithium storage applications e.g. Li-ion batteries has been considered.

In this ground, foamed Ag substrate has been used for EPD process to deposit CNTs inside its pores. By this method, it is expected a higher amount loading of the CNTs and also better interconnections between them and the silver frame.

On the other hand, Chronopotentiometry measurements show that i): Li storage capacity of the foamed silver is several times more than the plane Ag electrode, ii): the prepared Ag-CNTs working electrodes have very notable functional stability during successive C&D cyclic applications without any disintegration of the CNTs from the foamed silver frame. Because the porous structure of the electrodes have ability to buffer the volume variation of the electrodes during lithium charging (expansion) and discharging (contraction) periods.

In addition, by scanning the regulated current from 0.2 up to 1 mA, there was a convergence between C&D cyclic voltage profiles in the range of 0.4–0.6 mA and also, an optimization on reversible Li storage capacity has been observed in this range for the electrodes. This optimized behavior of the prepared electrodes could be interpreted as a result of dependency of the SEI film formation (near surface of the Ag-CNTs electrode) to the regulated current values during the C&D cycles.

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