Chapter 4

Nanocrystalline Co$_3$O$_4$ in Li-ion Batteries and Supercapacitors

4.1 Introduction

The ever growing need for better energy storage materials demands compelling improvements in the primary energy technology sector such as batteries, fuel cells, solar cells and supercapacitors. Among them Li-ion batteries (LIB) represent one of the dominant candidates for mobile phones and portable applications, due to their high energy density, modularity and long cycle life [1–5]. The present generation of LIB, however, uses expensive components that will restrict the growth of LIB in the next decade, urging researchers to develop better materials that are cheaper and more efficient. Transition metal oxides are known to have, in principle, higher capacity but suffer major set backs in the perspective of cycle life [6–8]. On the other hand, the commercial batteries use carbonaceous materials as the negative electrode that have shown reasonable cycle life despite posing severe restrictions on the maximum attainable energy density (<372 mAhg$^{-1}$) along with staging and fading of capacity that is commonly observed in these electrodes [9]. This prompted the need for immense research on alternate electrode materials, from a wide variety of compounds ranging from metal oxides and intercalation compounds of transition metals to nanostructured materials such as Si/Sn based nanowires and hybrid materials like LiFePO$_4$ [10–15]. In the case of nanostructured materials, different morphologies, such as nanowires, nanotubes and nanorods, tend to give varying energy density due to their preferred orientational features [16–20].

The tremendous growth in the consumption of energy resulted in an urgent need for efficient energy conversion and storage. While fuel cells and batteries offer higher energy
density, they cannot offer very high power density. On the other hand, electrochemical supercapacitors provide higher power density when compared to the Li-ion batteries. The simplified Ragone plots (see Figure 1.13 in chapter 1) clearly reveal that to match the performance of internal combustion engines, a hybrid between supercapacitors with fuel cell and/or batteries is necessary [21]. Further, supercapacitors are suitable for many applications such as hybrid electric vehicles, uninterrupted power supplies and backup power sources for computer memory due to their higher power density and longer cycle life. Supercapacitors are generally of two types, electric double layer capacitors (EDLCs), where non-faradaic processes are the key for energy storage while in pseudo-capacitors, the redox process of the active material contributes for the capacitance. The application of RuO$_2$.xH$_2$O as an electrode material marked a new breakthrough in pseudo-capacitors that brought the attention towards various transition metal oxides such as NiO, MnO$_2$, and Ni(OH)$_2$ for electrode applications [22–24].

Among transition metal oxides, Co$_3$O$_4$ with selective shapes has recently been shown to be a promising anode material for LIB technology [25–28]. The inherent advantages of the needle like structures obtained through a virus enabled synthesis route is utilized for increased capacity [26]. Similarly, the influence of shape over the capacity has been demonstrated [29]. After proving its utility as an anode material in Li-ion batteries, Co$_3$O$_4$ has also prompted the research on its supercapacitive behavior due to the presence of redox couple to show pseudocapacitive behavior [30,31]. An important criterion to improve the energy density of any transition metal oxide based electrode is to improve the electrode-electrolyte interface by means of reducing the particle size and increasing the porosity [31].

Hence, the Co$_3$O$_4$ porous nanorods prepared by a template free simple and facile coprecipitation/digestion method, as described in the previous chapter (the sample CC-300) has been tested as an anode material in the LIB application and also evaluated for its performance in a supercapacitor.

4.2 Application as anode in LIB

For the evaluation of Co$_3$O$_4$ as the anode material for rechargeable LIB, a mixture of Co$_3$O$_4$ obtained by calcining the precursor at 300 °C (CC-300), Vulcan XC-72 carbon and Nafion taken in the ratio of 75:20:5, was brushed on a stainless steel 316 (SS) mesh.
and it was used as the working electrode. Li metal served as the counter and reference electrodes with 0.1 M LiClO$_4$ in propylene carbonate (PC) as the electrolyte.

To get detailed information on the characteristics and properties of the CC-300 electrode, various characterization techniques such as XRD, HRTEM, solid state NMR and magnetic measurements have been carried out. The cyclic voltammogram (CV) and impedance measurements were carried out on Autolab 30 PGSTAT and Solartron instruments, respectively. Charge-discharge experiments were carried out on a home made galvanostatic set up using a Keithley 6514 electrometer and 2010 multimeter connected in series with a variable resistance box. All the experiments were carried out in argon atmosphere. Magnetic measurements were carried out on a vibrating sample magnetometer.

Figure 4.1 shows the cyclic voltammogram (CV) of single cell assembly utilizing the porous Co$_3$O$_4$ nanorods (CC-300). The CVs are measured at a scan rate of 1 mV/s over the potential window of 0-3 Volt. Two anodic peaks and one cathodic peak are observed.
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and this may be attributed to the Li ion insertion and desertion in the Co$_3$O$_4$ matrix. More specifically, the anodic peaks can be ascribed to the oxidation of Co concomitant to the intercalation of Li$^+$ on to the Co$_3$O$_4$ matrix where as the cathodic peak observed at 0.7 V could be attributed to the reduction of Co$_3$O$_4$. This is in accordance with literature reports of Co$_3$O$_4$ reduction [26, 27]. For example, Nam et al have proved that the reduction of Co from higher to lower oxidation state occurs at $\sim$0.7 V and Au support is shown to be positively influencing the cathodic peak of Co$_3$O$_4$ prepared through a virus enabled root [26]. The control experiments carried out with stainless steel 316 mesh did not show any peak in the CV, and this further confirms that the peaks originate from the Co$_3$O$_4$ nanorods only.

The open circuit potential (OCP) measured for the porous sample CC-300 coupled with a Li metal foil is 3.6 V which is in very good agreement with the reported values. Figure 4.2 shows constant current discharge curves using lithiated CC-300 as the anode. After an initial drop from the OCP, the potential follows a two step discharge to reveal

Figure 4.2: Galvanostatic discharge curves of the sample CC-300 measured at a discharge rate of 50 mAh$^{-1}$ using LiClO$_4$ dissolved in propylene carbonate as electrolyte.
a complete capacity of 1155 mAh$^{-1}$ which is significantly higher than that of the carbonaceous electrodes used in commercial batteries (providing ca. 372 mAh$^{-1}$) and other Co$_3$O$_4$ based Li ion electrodes (≈850-700 mAh$^{-1}$) \[28,32\].

For the effective application of any material used as an anode in the rechargeable Li-ion batteries, the number of cycles the electrode is able to withstand at the constant discharge rate is important for its usage in practical applications. Hence, the sample CC-300 had been subjected to the cycle life measurements at the constant discharge rate of 50 mAh$^{-1}$. Interestingly, the cycle life measurements shown in Figure 4.3 reveal that after dropping from a capacity of 1155 to 908 mAh$^{-1}$, the capacity of the Co$_3$O$_4$ becomes steady at 820 mAh$^{-1}$ for more than 25 cycles, which is still much higher than that of commercial carbon based electrodes. This abides well with the fact that structures with smaller transport pathways will give better Li insertion due to decreased volume change which is expected to give improved capacity and cycle life \[20,28\].

Figure 4.4 shows the XRD patterns of the CC-300 electrode material before and after
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Figure 4.4: Comparison of the XRD patterns of CC-300 with that of the material after discharging (CC-300-D) and charging (CC-300-C).

the charge-discharge cycles. It is observed that the XRD patterns of the charged and discharged samples do not show any noticeable changes when compared to that of the pristine material, demonstrating the stability of the nanorod matrix.

In general, the possible operating mechanism for a metal oxide reacting with Li is the formation of nanodomains of metal and Li$_2$O in the metal oxide matrix during discharge and reversion of the oxide while charging back [33]. In the case of Co$_3$O$_4$ also, it is reported that there is formation of Co nanodomains with Li$_2$O during discharge and formation of $\beta$-CoO instead of Co$_3$O$_4$ while charging back. For example, Li et al confirmed the formation of Co through the observation of dark grains in the HRTEM image with the lattice fringe value corresponding to the structure of Co. Their XRD pattern showed broad and weak reflections due to Li$_2$O and fcc Co [34]. However, peak due to Li$_2$O is not observed in the XRD patterns shown in Figure 4.4, indicating that probably very fine (amorphous) nanosized Li$_2$O is formed.

Since there are no peaks in the XRD pattern corresponding to Li$_2$O are observed, changes in the Li environment during discharge was probed through $^7$Li solid state NMR.
Figure 4.5: \(^7\)Li solid state NMR of CC-300 after discharge, compared with lithium chloride as reference.

Figure 4.5 depicts the \(^7\)Li NMR spectra of the discharged sample CC-300-D. It clearly shows a chemical shift of \(\sim 2\) ppm against LiCl. This result confirms the formation of \(\text{Li}^+\) during the discharge (insertion), as the chemical shift resembles more towards the \(\text{Li}^+\) than towards the metallic Li (\(\text{Li}^0\) state) [16].

HRTEM images of the charged (CC-300-C) and discharged (CC-300-D) samples are shown in Figure 4.6. The images are not clear probably due to the formation of a polymeric film from the electrolyte and also due to the solvent adsorption and intercalation in the pores. As per the reported mechanism [34], formation of Co nanodomains in \(\text{Li}_2\text{O}\) matrix is expected.

Since the presence of Co is not observed in the XRD pattern, the inherent advantage of magnetic measurement is used, which is an effective and sensitive tool to confirm even trace amounts of Co since it is ferromagnetic. From Figure 4.7 it is very clear that the discharged sample CC-300-D shows a ferromagnetic response to the applied field which is a confirmation for the formation of Co nanodomains which are ferromagnetic in nature. The inset in Figure 4.7 shows the response of the samples CC-300-C and CC-300 to the
Figure 4.6: HRTEM images of the (a) discharged (CC-300-D and (b) charged (CC-300-C) samples.

Figure 4.7: M vs H measurement of CC-300-D. Inset: M vs H curves of CC-300-C and CC-300.
applied field. The bare sample and the charged one do not show any ferromagnetic signal since Co$_3$O$_4$ is paramagnetic at room temperature. Also, the magnetic measurements reveal that the amount of Co is very less in the discharged sample from its magnetization value of 0.36 emu/gm. For Co nanoparticles of size in the range of $\sim$10 nm, magnetization value of 20 emu/g is reported against the bulk value of 160 emu/g. This corresponds to less than 1% of Co nanoparticles in CC-300-D, which proves the stability of the material.

A two-step structural modification is anticipated in the Co$_3$O$_4$ matrix with initial insertion of Li, which on further Li desertion regains the original structure. Even after 10 charge-discharge cycles, the material is not completely converted into metallic Co, as inferred from the XRD and magnetic measurements. This can be attributed to the stability of the material and the shorter pathways offered by the highly porous structure. Further, it could also be due to the formation of more and more active sites that would be regenerated by the redox process which is favored here due to the structural aspects of the material.

Hence, it can be concluded that the as-prepared porous nanorods of Co$_3$O$_4$ is highly stable with more active sites. The material shows a considerably good specific capacity of 1155 mAhg$^{-1}$ and further stabilizes with a value of 820 mAhg$^{-1}$ for more than 25 cycles.

### 4.3 Application as a supercapacitor material

To study the supercapacitive behavior of the porous CC-300 nanorod sample, cyclic voltammogram (CV) in alkaline medium was measured using 6M KOH solution as the electrolyte. The sample was coated on a carbon paper which serves as the working electrode while Pt wire and foil were used as the reference and counter electrodes, respectively. Figure 4.8 clearly reveals a highly pseudo-capacitive behavior of the CC-300 electrode. The observed reversible electrochemical behavior, in addition to the almost rectangular CV shape, is ideal for a pseudo-supercapacitor due to contributions from both faradaic and non-faradaic processes [35]. The redox peak observed for the Co$^{2+/3+}$ couple is playing a crucial role in improving the capacitance of the electrode. The capacitance value calculated from the CV is 510 Fg$^{-1}$ which is much higher than the reported value of 450 Fg$^{-1}$ [30] and 95 Fg$^{-1}$ [36] for Co$_3$O$_4$ nanorods and micro porous nanostructures. The higher value obtained here could be attributed to the enhanced surface area and higher
porosity of the nanorods which improve the electrode-electrolyte interface.

Figure 4.9 shows the scan rate dependant CV of the CC-300 electrode in KOH medium. The figure clearly reveals the quasi-reversible behavior of the CC-300 nanorods which is well known for the Co$_3$O$_4$ based systems. A plot of specific capacitance vs scan rate is shown in Figure 4.10. The specific capacitance measured at different scan rates show significant reduction in the capacitance value at higher scan rates. This mainly originates from the quasi-reversible nature of the material and the 3D nature of the pores since at high scan rates the deep insides of the pores can not be accessed.

To get the in depth information about the capacitive nature of the Co$_3$O$_4$ nanorod based electrodes, charge-discharge (CDC) experiments are carried out. The charge-discharge (CDC) experiment is carried out in 6 M KOH electrolyte with the charging-discharging rate equivalent to a current density equivalent of 1 A/g. Figure 4.11 shows the calculated capacitance value with CDC cycle number. The region of the curve from 0.1 to 0.6 V on the y-axis represents the electrochemical redox reaction. The capaci-
Figure 4.9: Comparison of the cyclic voltammetry curves of porous CC-300 measured at different scan rates.

Figure 4.10: Scan rate dependent capacitance of CC-300 nanorods.
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Figure 4.11: Galvanostatic charge-discharge curve obtained for porous CC-300 nanorods at various cycles - 2nd, 500th and 800th cycle confirming the cycle stability of the electrode. The capacitance is measured from the slope of the curve given by $I \times \Delta t/\Delta V \times m$, where $I$ is the galvanostatic discharging current, $\Delta t$ is the discharging time, $\Delta V$ is the potential drop during discharge, and $m$ represents the mass of the electroactive material. The obtained capacitance value is found to be quite high with the value of 600 F g⁻¹ that is in close agreement with the capacitance calculated from the CV measurements. Further, these values are also close to the capacitance value of state of art material RuO₂ (720 F g⁻¹).

Another important issue is the cycle life. Co₃O₄ based materials are normally known for their poor durability [37]. The CDC curves for the 2nd, 500th and 800th cycles shown in Figure 4.11 confirm that there is no significant variation in the capacitance even after 800 cycles of CDC operation. One interesting observation is that, with cycle number, the contribution of electric double layer charging also increases significantly suggesting the increased pore openings and higher accessibility. This is in accordance with the very high surface area and highly porous nature of the CC-300 nanorods which allows very short paths for the ions to reach the interior and thus keeps the integrity of the material intact.
Figure 4.12: Response of CC-300 discharged at different current densities.

Figure 4.13: Impedance spectroscopy analysis of porous CC-300 nanorods.
The material CC-300 has also been tested at different discharge current densities as shown in Figure 4.12. The figure clearly shows the trend of decrease in the response time as there is an increase in the discharge current densities. The results are well in agreement with the CV data, as at higher CDC rates the capacitance is observed to be low and able to deliver the charge in few seconds. The electrochemical impedance spectroscopy analysis was carried out in the frequency range of 0.01 to 1 MHz with ac voltage amplitude of 5 mV to further substantiate the capacitive performance of CC-300 material at the open-circuit potential. The typical Nyquist plot of CC-300 electrode before and after CDC is shown in Figure 4.13. From the high frequency intercept at the x-axis, one can calculate the electrode-electrolyte total system resistance. An initial resistance value of 28.7 Ω is reduced to 1.7 Ω after CDC experiments, revealing the increased exposure of the pores due to the prolonged operation. This fact further emphasizes that initially not all the pores in the electrode are used for charge storage and also at very high scan rates. However, at low scan rates, majority of the pores could be accessed that result in higher capacitance values.

4.4 Conclusions

The porous Co$_3$O$_4$ nanorods are demonstrated to have a capacity of 1155 mAhg$^{-1}$ in Li-ion battery, during initial cycles, followed by excellent durability of providing the capacitance value of 820 mAhg$^{-1}$ for 25 cycles and beyond with out any obvious signs of capacity loss or performance degradation. The reason behind this enhanced capacity is probably due to the porous nature of the nanostructured material, which results in reduced volume change upon insertion/deinsertion, which also results in better cycle life. Solid state NMR study confirms the change in Li environment during the discharge process. The XRD measurements after charge and discharge prove the stability of the material and at the same time the formation of Co nanodomains has been confirmed by magnetic measurements. Also the material exhibited a considerably quite high value of capacitance (600 Ag$^{-1}$) during the galvanostatic discharge measurement, indicating the applicability of porous nanorods of Co$_3$O$_4$ as a suitable material for supercapacitor applications.
References


[34] Y. Li, B. Tan, Y. Wu, Nano lett. 8 (2008) 265.

