

Electrochemical characterization of a polypyrrole/ $\text{Co}_{0.2}\text{CrO}_x$ composite as a cathode material for lithium ion batteries[☆]

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Abstract

Polypyrrole/ $\text{Co}_{0.2}\text{CrO}_x$, (PPy/ $\text{Co}_{0.2}\text{CrO}_x$) composites were synthesized by polymerizing pyrrole onto the surface of cobalt chromium oxide (CrO_x) in acidic media. The PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composites increase the reversible capacity of the electrochemically active material up to 20%. At $C/10$ rate, a reversible capacity of 215 mAh/g was obtained for PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composite, compared to 178 mAh/g for the virgin material, an increase of over 21%. Conductivity experiments corroborated the galvanostatic cycling tests, with the composite cathode material showing high electronic conductivity than bare material. Fitting the impedance results to an equivalent circuit reveals that addition of polypyrrole reduces the ohmic resistance due to the better conductivity and the inclusion of electrochemically active polypyrrole in the composite. Finally, the composite electrodes also showed very good rate capability and better cycling behavior compared to that of the bare material. © 2003 Elsevier B.V. All rights reserved.

Keywords: Polypyrrole; Lithium ion batteries; Chromium oxides

1. Introduction

Chromium oxides (CrO_x) are promising cathode materials for secondary lithium batteries [1,2]. Recently Arora et al. [1] showed that they exhibit high initial capacity (240 mAh/g). However, both lithiated and non-lithiated chromium oxides exhibit large capacity fade during cycling and also show poor rate capability. Low rate of lithium transport in these oxides hinders their performance at higher discharge rates [3,4]. In our previous work, we developed an alternate synthesis procedure to improve the electrochemical characteristics of the CrO_x material [5]. The new synthesis technique reduced the capacity fade during cycling but did not change the rate capability significantly. Zhang et al. [6] found that doping cobalt into CrO_x improves the high rate discharge behavior of chromium oxides. They also have optimized the content of cobalt in CrO_x as $\text{Co}_{0.2}\text{CrO}_x$. However, the specific capacity of $\text{Co}_{0.2}\text{CrO}_x$ is less than the virgin CrO_x material, due to the doping of cobalt into CrO_x particles.

Research was extended in order to identify new dopants, which would improve the high rate discharge characteris-

tics while retaining or improving the specific capacity of these materials. Electronically conducting polymers such as polypyrrole, polyaniline and polythiophene have attracted attention as electrodes in batteries and super capacitors [7,8]. Polyaniline and polypyrrole (PPy) have been used in lithium ion batteries [9,10]. Apart from being electrochemically active, they also act as a conducting additive, thereby reducing the inert weight associated in the preparation of the electrode. The redox reaction of the polypyrrole and the consequent lithium intercalation serves as the source of the capacity during cycling. Kuwabata et al. [11–14] have doped polypyrrole into MnO_2 , LiMn_2O_4 , V_2O_5 , etc. and found that the doping improved the performance of these cathode materials. They also found that polypyrrole is electrochemically active in the region 2.0–4.3 V versus Li/Li^+ and possesses a theoretical capacity of 64.5 mAh/g. They observed that the incorporation of polypyrrole in these cathode active materials improves the conductivity and thus improves the high rate discharge behavior. Pasquier et al. [15] found that the polymerization of pyrrole with LiMn_2O_4 in acidic medium causes surface modification of the spinel oxide, which prevents the cathode from further capacity fading.

In this work, we attempted to incorporate polypyrrole into $\text{Co}_{0.2}\text{CrO}_x$ and tried to improve the electrochemical characteristics of the composite. With the help of electrochemical characterization techniques, we found that the incorporation of PPy onto $\text{Co}_{0.2}\text{CrO}_x$ results in higher specific capacity,

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better high rate discharge behavior and better conductivity over bare $\text{Co}_{0.2}\text{CrO}_x$ materials.

2. Experimental

2.1. Composite synthesis

Crystalline $\text{Co}_{0.2}\text{CrO}_x$ was prepared by heating a mixture of CrO_3 (99.5% Alfa Aesar), $\text{Co}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ (99.9% Alfa Aesar) and a small amount of $(\text{NH}_4)_2\text{SO}_4$ (99% Aldrich), inside an autoclave for 48 h under high oxygen pressure of 500 psi. Care was taken that the temperature was maintained in the range 270–290 °C.

2.2. Incorporation of polypyrrole

Polypyrrole was then incorporated into $\text{Co}_{0.2}\text{CrO}_x$ active material by injecting liquid pyrrole monomer into a 1 M HClO_4 aqueous solution containing various amounts (2, 1.5, 1, 0.5, and 0.25 M) of suspended $\text{Co}_{0.2}\text{CrO}_x$, so as to give 0.1 M of pyrrole in the solution. Prior to the addition of pyrrole the suspension was bubbled with nitrogen gas for 15 min [12]. Enough time was allowed for the polymerization reaction to occur completely. After stirring the suspension for 30 min, the composite in the polymerization bath was collected by filtration and then washed with 1 M HClO_4 , then with de-ionized water several times and then finally with acetonitrile (99.5% Aldrich) in a vacuum suction filter using Fisher P8 filter paper. The purified samples were then dried in vacuum (Yamato ADP-21 oven) at 120 °C for 12 h to remove traces of water.

2.3. Material characterizations

Thermogravimetric analysis (TGA) was used to determine the change in weight of the composites with increase in temperature and to estimate the amount of polypyrrole in them. Thermogravimetric analysis was performed in a Perkin-Elmer TGA7 Thermogravimetric Analyzer in argon filled glove box and the samples were heated from room temperature to 650 °C at a slow scan rate of 5 °C/min. The polypyrrole decomposes and vaporizes at a temperature of 420 °C and the weight loss of the sample at that temperature directly translates into the amount of polypyrrole in the composite. The morphology of the composites was analyzed using a Hitachi S-2500 Delta Scanning Electron Microscope (SEM).

2.4. Electrode preparation

Subsequent to drying the active material ground to fine powder and then sieved through 100 μm sieves. For preparing disc electrodes the active material was mixed with 10% carbon black (Alfa Aesar, conducting additive, 99.9% pure, 80 m^2/g) and 5% PTFE (binder) and then pressed into a thin film (50–60 μm thickness). Pellets of 1 cm diameter

and about 15 mg weight were prepared for electrochemical studies.

2.5. Electrochemical characterizations

All electrochemical studies were done in a Cole–Parmer three electrode cell assembly (T-cells). Discs of the composite being tested were used as the working electrode while pure lithium foil (FMC Corp.) served as the counter and the reference electrodes. The separator was a sheet of Celgard 2340 μ porous separator. The electrolyte used in this study was 1 M LiPF_6 in a 1:1 mixture of EC and DMC. The entire cell assembling was carried out in a glove box filled with dry argon and once the cells were assembled, they were left in the dry box for about 1 h, to make sure that the electrolyte diffuses into the porous structure of the cathode.

The galvanostatic charge–discharge cycling was carried out in an Arbin BT-2043 Battery Test Station at a low current density of 0.3 mA/g ($\sim C/10$ rate), with the cut-off potentials being 2.0–4.2 V versus Li/Li^+ . For studying the rate capability of the composites, charge discharge curves were obtained using different current rates in the same potential range. Electrochemical impedance spectroscopy (EIS) experiments were carried out using a Solatron 1255 Frequency response analyzer along with EG&G potentiostat (Model 273A) between frequency limits of 100 kHz to 10 mHz, with a signal amplitude of 5 mV peak-to-peak.

3. Results and discussions

3.1. Estimation of the amount of polypyrrole in the composite

Thermogravimetric analysis has been used to quantify the amount of polypyrrole in the composite materials [16]. TGA analysis was done in argon filled glove box, with the temperature being scanned from room temperature to 650 °C at a rate of 5 °C/min. Fig. 1 shows the TGA analysis of

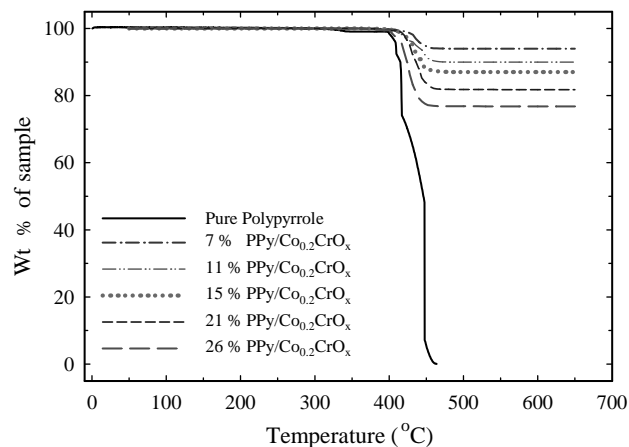


Fig. 1. TGA analysis of bare PPy and $\text{PPy}/\text{Co}_{0.2}\text{CrO}_x$ composites at a scan rate of 5 °C/min under air atmosphere.

the composite PPy/Co_{0.2}CrO_x samples along with those of bare Co_{0.2}CrO_x and polypyrrole. As seen from the figure, bare polypyrrole decomposes completely at a temperature of 420 °C, while the bare cathode material (Co_{0.2}CrO_x) remains stable in the temperature range used in the experiment. It can also be seen from the figure that the composites show weight loss at a temperature of 420 °C, which corresponds to the oxidation of polypyrrole [16]. There is no further weight change in the composites after the initial oxidation of polypyrrole, which shows that the base material remains unaffected after this initial weight loss. The difference in weight before and after oxidation of polypyrrole was determined and this change in weight directly translates to amount of polypyrrole in the composite. The amount of polypyrrole, in percentage, was found by subtracting the weight percentage of the bare graphite at 420 °C (100%) and that of the corresponding composite at the same temperature. This method is fairly accurate as the bare sample corresponding to Co_{0.2}CrO_x is stable up to 650 °C. Using this method, it was found that the amounts of polypyrrole in the composites varies from 7 to 26 wt.%.

3.2. Charge–discharge behavior of composites

Fig. 2 shows the initial lithiation of PPy/Co_{0.2}CrO_x composites under galvanostatic cycling. The behavior of bare Co_{0.2}CrO_x has also been shown for comparison. It must be noted that the capacity is based on the total weight of the electrode (binder + polypyrrole + Co_{0.2}CrO_x). The potential range used in the cycling experiment (2.0–4.2 V versus Li/Li⁺) is associated with the reversible lithium intercalation into the Co_{0.2}CrO_x structure. As seen from Fig. 2, the capacity associated with the initial lithiation of bare Co_{0.2}CrO_x material is 221 mAh/g. The plot also shows the initial lithiation behavior of PPy/Co_{0.2}CrO_x composites in the same potential range. Polypyrrole has been shown to be active in the potential range 2.0–4.2 V versus Li/Li⁺. However, the capacity for lithium intercalation in the case of polypyrrole is far lower (–65 mAh/g) [13] than that of

Co_{0.2}CrO_x material assuming that the polypyrrole is fully utilized. Hence, it can be expected that an increase in the polypyrrole content in the composite would actually reduce the specific capacity that can be realized from the composite material. It can be seen from Fig. 2 that the lithiation capacities of 7% PPy/Co_{0.2}CrO_x and 11% PPy/Co_{0.2}CrO_x are higher than that of bare Co_{0.2}CrO_x while the lithiation capacities of 16% PPy/Co_{0.2}CrO_x, 21% PPy/Co_{0.2}CrO_x and 26% PPy/Co_{0.2}CrO_x are lower than that for the bare Co_{0.2}CrO_x. The initial increase in specific capacity could be due to the increase in conductivity of the composite. This reasoning can be supported by further analysis of the lithiation curves in Fig. 2, which shows that the initial potential drop during lithiation for bare Co_{0.2}CrO_x is larger than that of the composites. These results suggest that the addition of polypyrrole improves the conductivity of the material, thereby reducing the polarization losses of the Co_{0.2}CrO_x the electrode material. However, it must also be noted that the capacity presented here has been calculated based on the total active material (PPy + Co_{0.2}CrO_x) in the composite. As mentioned above, the specific capacity for polypyrrole is far lower than that of Co_{0.2}CrO_x. Hence, continuous increase in the amounts of polypyrrole reduces the specific capacity of the composite, as seen in the case of composites with polypyrrole content of 16 wt.% and above.

Another interesting feature that can be seen in the graph is that for PPy/Co_{0.2}CrO_x composites, lithiation occurs at a higher potential window than that of bare Co_{0.2}CrO_x. This characteristic would directly translate into a higher energy power density for a given applied load. This can be seen from the Ragone plot for bare and 11% PPy/Co_{0.2}CrO_x composite as shown in Fig. 3. It can be readily seen from Fig. 3 that for any given energy density the composites possess superior power density than bare Co_{0.2}CrO_x material. It can be summarized from the results of Figs. 2 and 3 that the addition of polypyrrole results in the decrease in polarization losses of the material, thus leading to better lithium intercalation characteristics with higher specific capacity and power density.

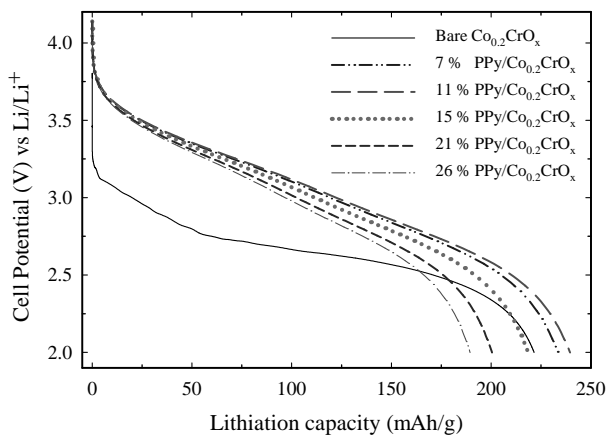


Fig. 2. Initial galvanostatic charge–discharge curves of bare and polypyrrole composite Co_{0.2}CrO_x samples in 1M LiPF₆/EC/DMC at C/10 rate.

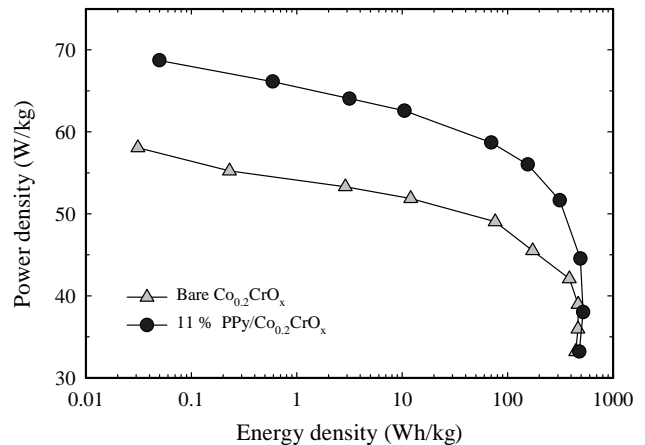


Fig. 3. Ragone plots for bare Co_{0.2}CrO_x and 11 wt.% PPy/Co_{0.2}CrO_x composite during initial lithiation.

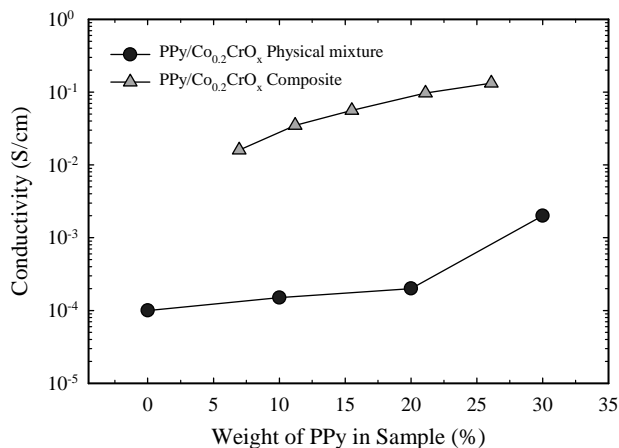


Fig. 4. Comparison of the conductivities of PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composite and physical mixture of polypyrrole and $\text{Co}_{0.2}\text{CrO}_x$.

The conductivity of electrode material is also an important factor in evaluating the performance of the electrode materials used in battery applications. In order to understand the decrease in the polarization losses as seen in Fig. 2, the conductivity of the samples were measured using a four probe method. In this technique, the material being studied is made into a thin film and its conductivity is measured by impressing a potential across two probes while simultaneously monitoring the current through the remaining two probes. In order to better understand the effect of forming composite polypyrrole on the conductivity of the samples, physical mixtures of PPy/ $\text{Co}_{0.2}\text{CrO}_x$ with varying amounts of PPy were prepared and their conductivities were measured. Fig. 4 shows the conductivity of the PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composites with that of the physical mixture. It can be readily seen from the plot that the conductivity of the composite continues to increase with the addition of polypyrrole. It can also be observed that the conductivity of the composite is superior to that of the physical mixture at all compositions by an order of magnitude. This can be expected as during composite formation, intimate mixing of the two components occurs, thereby reducing the interparticle resistivity and increases the electronic conductivity of the composite. This increased electronic conductivity manifests itself in better cycling performance of the PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composites as compared to bare $\text{Co}_{0.2}\text{CrO}_x$.

3.3. Impedance analysis of PPy/ $\text{Co}_{0.2}\text{CrO}_x$

Impedance analysis was done to study the effect of polypyrrole on the ohmic, interfacial and the polarization resistances of the composites during lithiation. Impedance experiments were performed after keeping the cells at their open circuit potential for 2 h in completely lithiated state. In order to ensure the uniformity of testing conditions, the electrodes were cycled galvanostatically for 10 cycles to ensure complete formation of surface films over the electrode particles. Fig. 5 shows the Nyquist plots of the composite

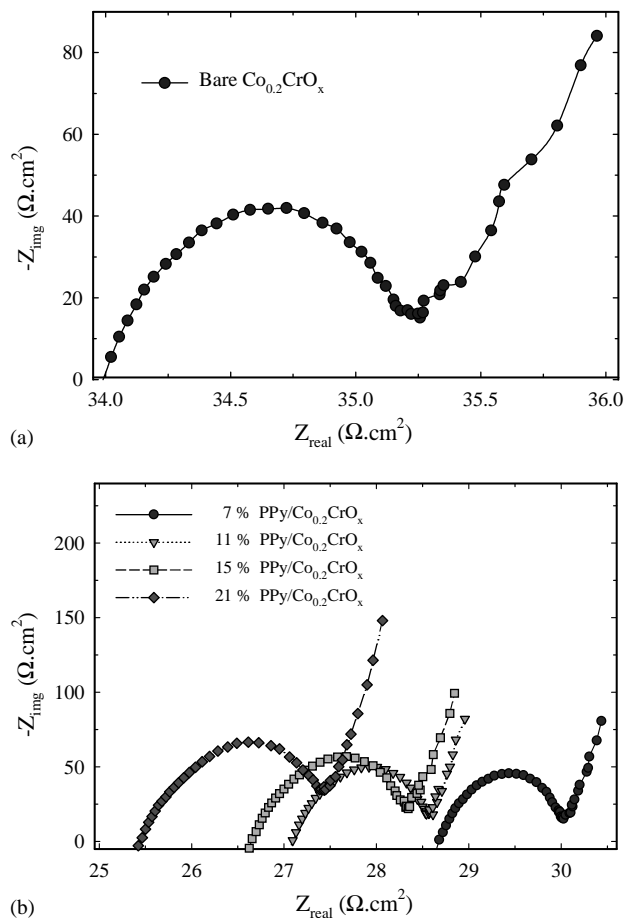


Fig. 5. (a) Impedance plots for the bare $\text{Co}_{0.2}\text{CrO}_x$ in the de-lithiated state between the frequencies 10 kHz and 10 mHz. (b) Impedance plots for the polypyrrole composite $\text{Co}_{0.2}\text{CrO}_x$ in the de-lithiated state between the 10 kHz and 10 mHz.

electrodes as compared to that of the bare electrode. It can be seen from the plot that the ohmic resistance of the composites is low when compared to that of bare $\text{Co}_{0.2}\text{CrO}_x$. This agrees with the conductivity results discussed earlier. The Nyquist plots for the electrode materials are composed of a semicircle in the high mid frequency region. According to previous studies, the high frequency region of the semicircle corresponds to the migration of the Li^+ ions through a surface film at the electrode/electrolyte interface and the mid frequency range of the semicircle is attributed to the charge transfer kinetics [17]. The low frequency region of the plot corresponds to the semi-infinite diffusion of the lithium ions into the bulk of the electrode material. Since there is no distinct separation in the shape of semicircle between the high and mid frequency regions, the charge transfer kinetics and the migration through the interfacial film cannot be distinguished as two separate processes. Hence, the entire semicircle can be attributed to the resistance to charge transfer reaction, which also includes the migration resistance offered by the interfacial film formed over the electrode surface. The figure shows that the ohmic resistance has decreased drastically for all PPy/ $\text{Co}_{0.2}\text{CrO}_x$

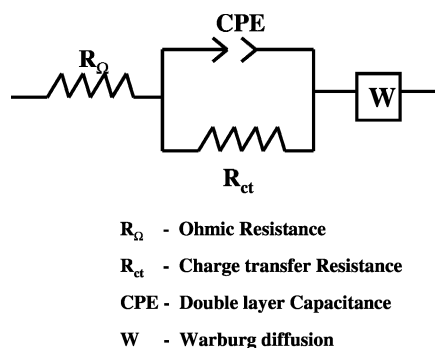


Fig. 6. Equivalent circuit used to fit the experimental impedance responses of the composites.

samples when compared to that of bare $\text{Co}_{0.2}\text{CrO}_x$, while there is a slight increase in the charge transfer resistance (although this increase is insignificant) as the polypyrrole content in the composite increases.

Fitting the experimental impedance results to an equivalent circuit can provide important information about the effects of various resistances. Careful examination of the magnified experimental impedance curves suggests that the Nyquist plots are either depressed semicircles or arcs of semicircles whose center is displaced from the real axis. The data can be compared with the impedance of a plausible electrical equivalent circuit by complex nonlinear least squares fitting (CNLS) to extract parameters (circuit elements) which can be related to physical processes which are likely to be present. Although we typically employ ideal resistors, capacitors and inductances in an equivalent circuit, actual real elements only approximate ideality over a limited frequency range. In this work, the impedance plots appear as depressed semicircles signifying deviation from ideality. To compensate for this deviation from ideality, a constant phase element was added to the equivalent circuit. The equivalent circuit used to fit the impedance response is shown in Fig. 6. In the equivalent circuit, a constant phase element is placed

Table 1
Electrode resistances obtained from equivalent circuit fitting of experimental data

Sample of $\text{Co}_{0.2}\text{CrO}_x$	R ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)
Bare	34.0	1.30
7% Ppy	28.6	1.49
11% Ppy	27.0	1.65
15% Ppy	26.6	1.97
21% Ppy	25.4	2.40

in parallel with an ideal resistor (reaction resistance). Further details about the equivalent circuit fitting and CPE can be obtained from literature [18].

The numerical values of the resistances for the different components for both bare $\text{Co}_{0.2}\text{CrO}_x$ and $\text{PPy}/\text{Co}_{0.2}\text{CrO}_x$ obtained by fitting the experimental results are given in Table 1. As seen from the table, addition of even 7% polypyrrole decreases the ohmic resistance of $\text{Co}_{0.2}\text{CrO}_x$ by 20%. The ohmic resistance includes both the solution resistance and the DC resistance. The results are in agreement with the conductivity results, which tell us that the polypyrrole $\text{Co}_{0.2}\text{CrO}_x$ composites possess superior conductivity than that of the bare oxide. However, the composite samples show sluggish kinetics when compared with that of bare oxides. Similar observations were reported by Song [19].

Scanning electron microscopy was used to analyze the change in the morphology of the composite due to the addition of polypyrrole. Fig. 7 shows the scanning electron microscopy pictures of bare $\text{Co}_{0.2}\text{CrO}_x$ and 11 wt.% $\text{PPy}/\text{Co}_{0.2}\text{CrO}_x$ composite at a magnification of 20,000 \times . The micrographs of $\text{PPy}/\text{Co}_{0.2}\text{CrO}_x$ composite show that the particles of $\text{Co}_{0.2}\text{CrO}_x$ are encapsulated in the matrix of polypyrrole, which are formed uniformly over the surfaces of the $\text{Co}_{0.2}\text{CrO}_x$ particles. This matrix reduces the particle-to-particle contact resistance and improves the conductivity of the composite.

Table 2 compares the specific capacity for lithium intercalation, electrode conductivities and the utilization of PPy

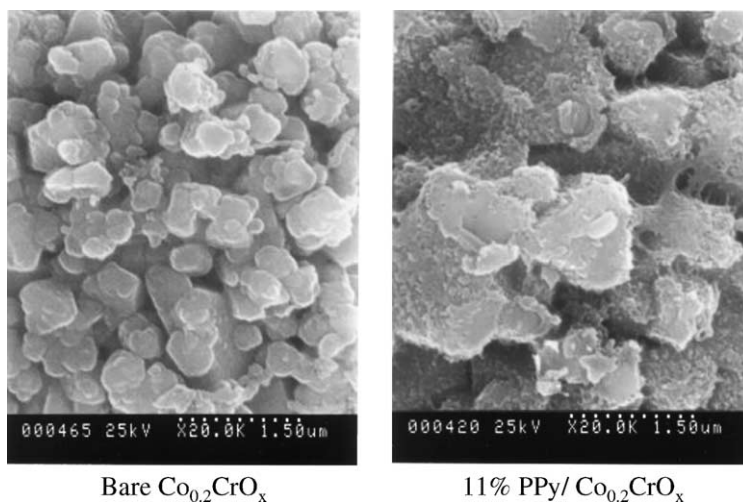


Fig. 7. Scanning electron microscopic pictures of bare $\text{Co}_{0.2}\text{CrO}_x$ and $\text{PPy}/\text{Co}_{0.2}\text{CrO}_x$ composites at a magnification of 20,000 \times .

Table 2

Electrode resistances obtained from equivalent circuit fitting of experimental data

Amount of PPy in composite	Conductivity ($\times 10^{-2}$) (S/cm ²)	Initial lithiation capacity (mAh/g)	Reversible lithiation capacity (mAh/g)	Specific capacity due to PPy (mAh/g) ^a	Utilization of PPy (%) ^b
Bare	2.36	221	178	–	–
7% PPy	3.91	231	189	25.2	39.1
11% PPy	4.12	242	215	45.8	71.0
15% PPy	4.31	215	183	28.3	43.8
21% PPy	4.46	198	162	23.6	36.7
26% PPy	4.59	181	140	17.7	27.4

^a Specific capacity due to PPy = specific capacity of composite – specific capacity of bare Co_{0.2}CrO_x.^b Utilization of PPy = (specific capacity due to PPy/theoretical specific capacity of pure PPy) \times 100.

in the prepared composites with that of bare Co_{0.2}CrO_x. It must be noted that the utilization of PPy has been calculated based on the theoretical capacity of PPy in the potential range 2.0–4.2 V versus Li/Li⁺ [13]. It can be seen from the table that the utilization of PPy increases with increase in polypyrrole amount in the composite up to 11 wt.%. This was expected because more amount of PPy is available for lithiation. However, with an increase in polypyrrole in the composite, more amount of PPy is coated over the same surface area of Co_{0.2}CrO_x particles resulting in layered coating of PPy over Co_{0.2}CrO_x particles. Hence, the utilization of PPy will decrease with an increase in PPy in the composite. This result can be seen from the table where an increase in PPy contents above 11 wt.% decreases the utilization of PPy in the composite. Even though the conductivity of the composite increases with increase in PPy amount in the composite, its specific capacity decreases due to less utilization of PPy as polypyrrole content increases. This can also be seen in Table 2. Based on the specific capacity, conductivity and utilization of PPy of the composites, it can be concluded that 11 wt.% represents an optimal amount of PPy in the composite and further analysis and comparison to bare Co_{0.2}CrO_x material was performed with composites containing 11 wt.% PPy.

3.4. Cycling behavior

Extended cycling studies were done on the T-cells containing bare and PPy/Co_{0.2}CrO_x electrodes to check the stability of the composite material. Previous studies done on polypyrrole by various authors show that the material is stable in the organic electrolyte used in Li ion cells. Kuwabata et al. have studied the effect of polypyrrole addition on Li ion cathode materials such as LiMn₂O₄ [13] and V₂O₅ [14]. Further charge–discharge studies conducted by Kuwabata et al. [13,14] reveal no loss in capacity with cycling for the composite electrodes. They also have reported that there is no adverse effect on the stability of the material in organic electrolyte. Boinowitz et al. [20] have studied the performance of polypyrrole as a negative electrode in a novel metal-free battery using LiClO₄ and propylene carbonate electrolyte. They also have observed no adverse effects on the stability of the material in organic electrolyte. These studies indicate that polypyrrole is chemically stable in Li

ion battery electrolytes. Fig. 8 presents the specific capacity of the bare Co_{0.2}CrO_x and 11% PPy/Co_{0.2}CrO_x electrodes (cycled at C/10 rate) as a function of number of cycles. As seen from the graph, the capacity fade observed in the case of PPy/Co_{0.2}CrO_x composite cathode is very less when compared with that of bare Co_{0.2}CrO_x. After 50 cycles, the capacity fade for the composite is less than 4% of its irreversible capacity, while that for the bare Co_{0.2}CrO_x this fade is 12%. This result can be expected in the case of the composites as better conductivity leads to better utilization of the active material resulting in lesser capacity fade with cycling. The study also reveals that the PPy included in the composite material is stable in the organic electrolyte during extended cycling.

3.5. Rate capability studies

Rate capability studies were done on 11 wt.% PPy composite and bare Co_{0.2}CrO_x electrodes to ascertain the performance of these materials under high rates of discharge. It is important to characterize these materials for their rate behavior, as most of the applications demand high-rate discharges during operation. Fig. 9 gives the percentage specific capacity of the electrodes for different applied loads. Percentage capacity was calculated based on the stable reversible capacity that correspond to the capacity observed

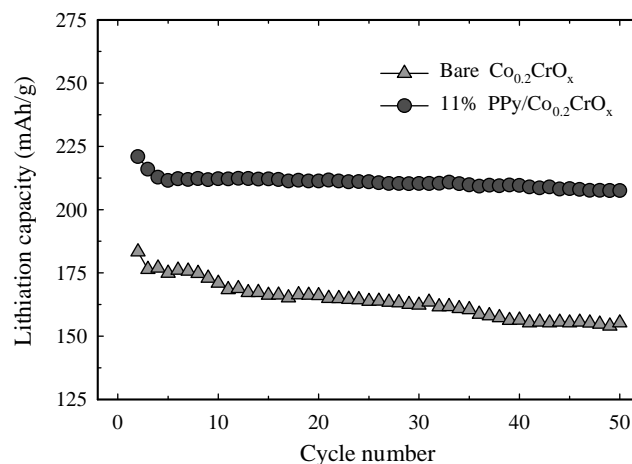


Fig. 8. Cycle life studies of bare Co_{0.2}CrO_x and 11 wt.% PPy/Co_{0.2}CrO_x composite samples at C/10 rate.

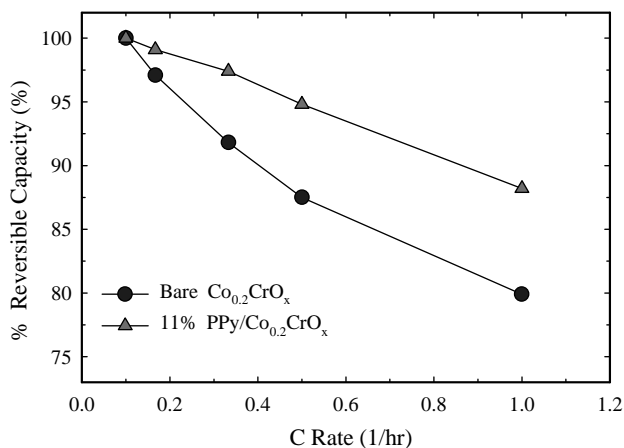


Fig. 9. Rate capability studies of bare $\text{Co}_{0.2}\text{CrO}_x$ and 11 wt.% PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composite samples as a function of discharge rates.

after complete formation (within three cycles) of the interfacial film. The values of the reversible capacity observed at $C/10$ rate are 221 mAh/g for $\text{Co}_{0.2}\text{CrO}_x$ and 242 mAh/g for 11% PPy/ $\text{Co}_{0.2}\text{CrO}_x$. The reversible lithiation capacities of the electrodes. As seen from the figure, the specific capacity of both these electrodes decreases at higher rates indicating the dependence of lithium intercalation on the mass transfer inside the electrode. However, the graph also shows that the composite electrode gives consistently higher capacity at all rates compared to the bare $\text{Co}_{0.2}\text{CrO}_x$. This can be expected as the conductivity of the electrode plays an important role in determining the high rate performance. The composite electrode retains 88% of their original capacity even at 1C rate whereas the bare $\text{Co}_{0.2}\text{CrO}_x$ could yield only 79% of its original capacity at the same rate. It is also noteworthy to study the capacity fade of these electrodes during cycling at higher discharge rates. The bare $\text{Co}_{0.2}\text{CrO}_x$ experiences more capacity fade at all rates as compared to the composite electrode. The capacity fade exceeds 40% when the bare oxide is cycled at 1C rate while for the 11% PPy/ $\text{Co}_{0.2}\text{CrO}_x$ this fade is just under 25%, which makes it reasonable to conclude that the PPy/ $\text{Co}_{0.2}\text{CrO}_x$ shows little or no deterioration due to high rate cycling. As mentioned in the previous studies, incorporation of polypyrrole improves the conductivity of the composite electrode and reduces the particle-to-particle contact resistance. The improved conductivity, as seen in EIS and conductivity results, could be the main reason behind the better rate capability of the composite electrode.

4. Conclusions

Pyrrole was polymerized onto $\text{Co}_{0.2}\text{CrO}_x$ material, to form PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composites. These composites are suitable for use as positive electrodes in rechargeable lithium ion batteries. Incorporation of PPy into $\text{Co}_{0.2}\text{CrO}_x$ materials up to a level of 11 wt.% increases the reversible capacity of the composites up to 20%. At $C/10$ rate, a reversible

capacity of 215 mAh/g is obtained for PPy/ $\text{Co}_{0.2}\text{CrO}_x$ composite, compared to 178 mAh/g for the virgin material, an increase of over 21%. Conductivity experiments corroborated the galvanostatic cycling tests, with the composite cathode material showing high electronic conductivity than bare material. Additional confirmation was obtained through complex-impedance spectroscopy. Fitting the impedance results to an equivalent circuit reveals that addition of polypyrrole reduces the ohmic resistance drastically due to the better conductivity and the inclusion of electrochemically active polypyrrole in the composite. Finally, the composite electrodes also showed very good rate capability and better cycling behavior compared to that of the bare material.

Acknowledgements

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