

# The Electrochemical Properties of Cu Coated $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$ Nanocomposites for High Rate Li-Ion Batteries

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Several reported problems of commercial  $\text{LiCoO}_2$  electrode materials such as high cost, toxicity, limited rate capability and safety concerns are still remain to be problematic to develop the lithium ion consumer electronics such as mobile phones, tablets and notebook computers. In this study, an alternative nanocomposite electrode material based on  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  and copper coated one were produced via a facile sol-gel method and electroless Cu deposition techniques. The resulting samples were characterized by X-ray diffraction (Rigaku DMax 2200 diffractometer) using a monochromatized Cu-K $\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ) and  $2\theta$  scan range from  $10^\circ$  to  $80^\circ$  with a speed of  $1^\circ \text{ min}^{-1}$ . The scanning electron microscope (SEM) was used in order to characterize the morphology of the active materials. The as-synthesized Cu/ $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  composite cathode exhibits a stable capacity on cycling and good rate capability after 50 cycles and total capacity retention of 93% is obtained. The unique 2D structure of the composite cathode material, its good electrochemical performances and its relatively low cost comparing to  $\text{LiCoO}_2$ , make this material very promising for applications.

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## 1. Introduction

The increasing demand for more reliable power sources for portable electronic devices and hybrid vehicles has drastically influenced the area of research for improved lithium-ion batteries electrode materials. Lithium-cobalt-based materials such as  $\text{LiCoO}_2$  are still most preferred cathode active materials in the rechargeable lithium ion batteries. However, when compared with the  $\text{LiCoO}_2$  electrodes lower cost, higher capacity and less toxic cathode electrodes are still needed in today's commercial batteries [1]. Although the  $\text{LiCoO}_2$  has a layered structure similar to the  $\alpha\text{-NaFeO}_2$  type structure (R3m space group), which provides a structural ability to reversibly intercalate lithium ions at high potential, these electrodes are mainly suffer from high cost, toxicity and instability at high potential windows. This capacity fade has been attributed due to several factors such as electrolyte decomposition, slow dissolution of  $\text{LiMnO}_2$  [2] unstable two phase reaction, Jahn–Teller distortion [3], lattice instability [4] and particle disruption [5]. Previous studies has shown that [6, 7] a couple of 5 V cathode materials obtained by substituting Mn in  $\text{LiMnO}_2$  with 3d transition metals such as Co, Cr, Cu, Fe, Ni, Ti and Zn, which are shown to be effective in suppressing the capacity fade upon cycling. In this regard, Cr and V as a dopant in  $\text{LiMnO}_2$  is also expected to exhibit an excellent electrochemical reversibility upon

cycling. In other words, reduced particle size that enhances the cycleability and rate capability of the positive electrode has also been aimed at in the present investigation. In recent years, several low-temperature preparation methods have been used such as sol-gel [1], precipitation [2], Pechini process [3, 4] and the hydrothermal method [5]. In this study, it is aimed to produce  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathode active electrodes by sol-gel method, using citric acid as a chelating agent with Cr and V as a dopant, which has not been previously reported. It should also be noted that soft chemistry such as sol-gel have many advantages such as better homogeneity, low calcinations temperature, shorter heating time, regular morphology, sub-micron sized particles, less impurities, large surface area and good control of stoichiometry. Therefore, a facile sol gel method has been employed to produce  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathodes in order to produce Cr-V-doped  $\text{LiMnO}_2$  solid solutions for improved lithium ion batteries. The as-synthesized powders were also coated with copper in order to enhance the electrochemical activities.

## 2. Experimental details

$\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  powder was produced via sol-gel method using citric acid as a chelating agent. 6 mmol of Manganese acetate tetrahydrate,  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was dissolved in deionized water to obtain a saturated solution. 10 mmol of lithium acetate dehydrate,  $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$ , 2 mmol of  $\text{Cr}_3(\text{OH})_2(\text{OOCCH}_3)_7$  (Alfa Aeser, 99.9%) and 2 mmol of Vanadium (IV) oxide bis (2,4 pentanedionate,  $\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$  (Alfa Aeser, 99.9%) were then added with mild stirring. A saturated aqueous citric acid was then added at a molar ratio of 12 mmol.

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pH of the final solution was kept at 7.0 by adding ammonium hydroxide. The solution was then heated to 90 °C with vigorous stirring to remove the excess ammonia and water until a transparent gel was obtained. The gel was then kept in air for 10 h oven at 120 °C in order to obtain metal citrate precipitation. After drying process, the precursors were decomposed at 850 °C for 6 h in air in order to eliminate organic contents.

The surfaces of the cathode active powders were pre-treated by using 1 M sodium hydroxide (Merck, Titripur) solution for 10 min and then  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  powders were then immersed into boiling hydrochloric acid (Merck, 1N) for 15 min to coarsen their surfaces. Then surfaces of the as synthesized powders were coated with copper after the powders were immersed in a palladium activation solution consisting of palladium dichloride (Merck,  $\text{PdCl}_2$ ) (0.3 g/l), stannous chloride (Merck,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , >99.9%) (16 g/l), sodium chloride (Merck, NaCl, >99.99%) (150 g/l) and hydrochloric acid HCl (Merck, 1N) (60 ml/l), and stirred strongly at room temperature for 15–20 min. The copper plating solution was composed of copper sulfate solution (28 g/l  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck, >99.9%, 30 g/l EDTA (Merck, Titriplex III), 14 g/l  $\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$  (Merck, >99%) and 10 mg/l  $\text{K}_4[\text{Fe}(\text{CN}_6)]3\text{H}_2\text{O}$ ] (Alfa Aesar, >98%) and formaldehyde solution (30 ml/l HCOOH (Merck, 37%), 100 ml/l  $\text{CH}_3\text{OH}$  (Merck, 99.5%) and 16 g/l NaOH). Plating was carried out at 30 °C in a container with ultrasonic bath (Bandelin Sonorex 10P). During the reaction process, NaOH (Merck, Titripur) solution was added until a pH value of 12 is obtained. Magnetic stirrer is necessary to make particles suspend in the solution and make the hydrogen produced during plating easily escape. After plating, the power was washed with distilled water and then dried in a vacuum oven at 80 °C for 12 h.

Electrochemical behavior during charge/discharge cycles was examined using a two-electrode test cell with lithium foil as the negative electrode. The positive electrode was a mixture of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  synthesized as above, conductive graphite and polyvinylidene fluoride in the weight ratio of 80:10:10. The resulting slurry was casted onto aluminum foil and dried at 140 °C for 8 h in vacuum. Cell assembly was carried out in an argon-filled glove box with an electrolyte of 1 M  $\text{LiPF}_6$  in EC-DMC (1:1 volume ratio) solution with Celgard 2400 as separator. The electrochemical data were collected using the MTI BST8A test system within the potential range of 3.0–4.3 V (vs.  $\text{Li}^+/\text{Li}$ ) at a constant current density of  $0.1 \text{ mA cm}^{-2}$ .

### 3. Results and discussion

The XRD pattern of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  powder is presented in Fig. 1. The diffraction lines in Fig. 1 clearly depicts that the as-synthesized powders could be indexed on the basis of  $a$  hexagonal lattice structure of  $\alpha\text{-NaFeO}_2$  with space group  $R\bar{3}m$ . No any other impurity phases were detected by XRD analysis and the narrowness of the diffraction lines indicate a good crystallinity. The

lattice parameters of the of the as-synthesized cathode active materials were also calculated via XRD results and found to be were  $a = 2.8144 \text{ \AA}$  and  $c = 14.3245 \text{ \AA}$ . The results have shown well-ordered layered structure of the  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  is produced. The surface modifying after Cu (111) and Cu (200) planes were also obtained showing that the  $\text{Cu}/\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  has successfully synthesized via electroless deposition techniques. The (006) and (104) peaks of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  is diminished due to formation Cu film over the surface  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$ . The X-ray has strong penetrating ability, thus, it can detect the  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  under the as-deposited coating. However, the intensity of the (006) and (104) diffraction peaks in the coated one diminished due to the partly absorbing of the incident and reflected X-rays by the as-deposited coating. It should be also mentioned that the relative intensity of (006) and (104) diffraction peaks were suppressed by the Cu (111) and (200) crystal planes when compared with the uncoated one in this study.

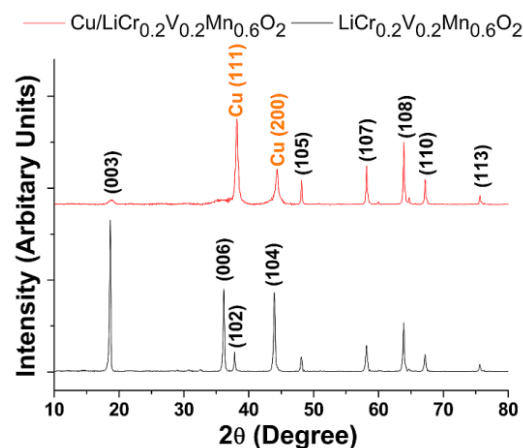


Fig. 1. XRD patterns of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  and  $\text{Cu}/\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathode electrodes.

The morphology of as-synthesized  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  powder is shown in Fig. 2. From the figures, it can easily concluded that the as-synthesized powders have well-shaped, polyhedron type crystals with the average grain size about 70 nm, which are very suitable for fabrication of the CR2016 batteries. Sub-micron particles have advantages for lithium batteries. The main advantages is the short path lengths for  $\text{Li}^+$  transport, short path lengths for electronic transport, higher electrode/electrolyte contact area leading to higher charge/discharge rates [6]. The electrochemical performance is known to be better when electrode materials are smaller in size because the insertion and de-insertion of lithium ions during the charge and discharge process can be facilitated. Energy dispersive spectroscopy (EDS) dot map analysis is also showing that the surfaces of the particles are successfully coated with Cu.

In order to examine the electrochemical reactivity and stability of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$ , 50 charge/discharge

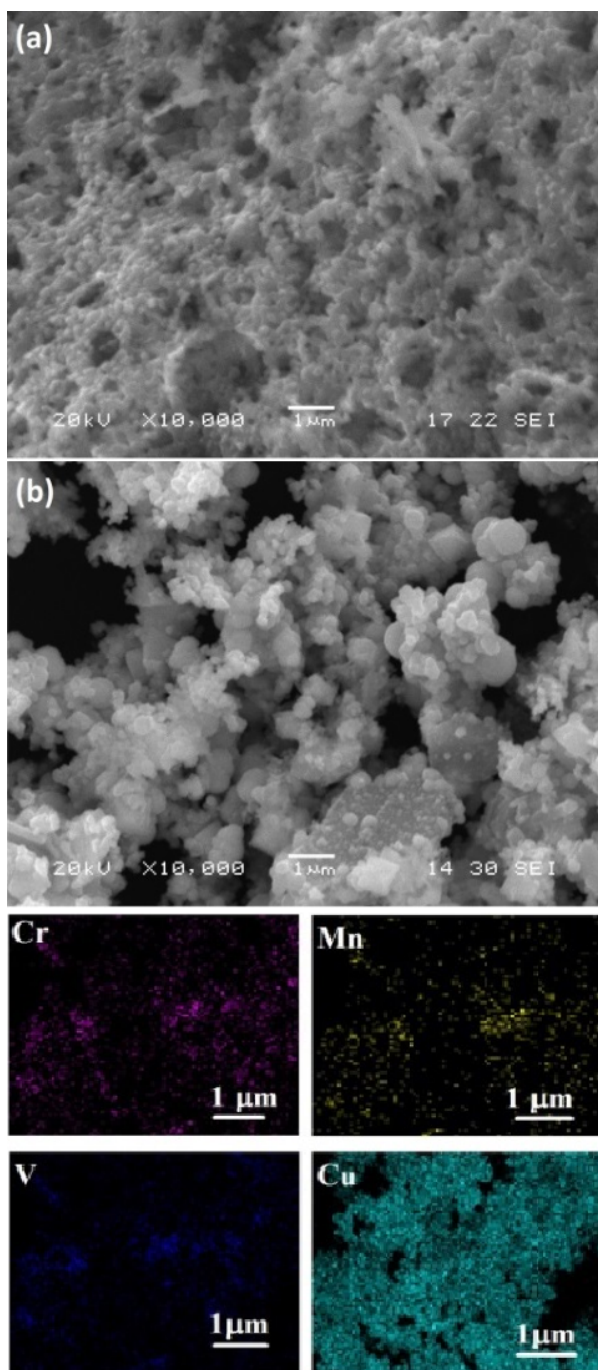


Fig. 2. SEM images of (a)  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  and (b)  $\text{Cu}/\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  with EDS dot map analysis cathode electrodes.

cycles were carried out under 1C rate, at room in the 3.0–4.3 V voltage range. As shown in Fig. 3a, it can be clearly observed that the capacity retention of the  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cell is 89.1% after 50 cycles. However,  $\text{Cu}/\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  composite structures have shown better results when compared with the non-modified  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cells as presented in Fig. 3b. A total capacity retention of 93% after 50 cycles was obtained after 50 cycles. The results have shown that

very stable cycling regime and remarkable cyclic performances of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  even at 1C charging and discharging conditions is obtained.

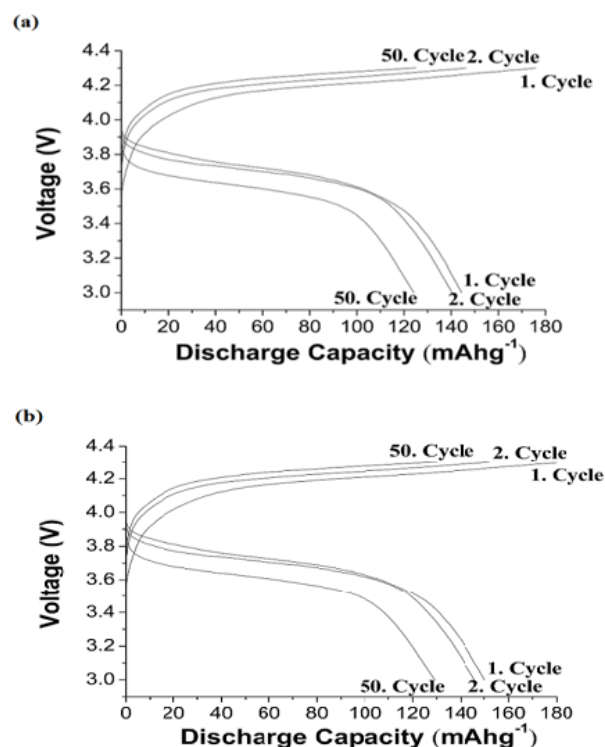


Fig. 3. Galvanostatic charge/discharge tests of (a)  $\text{LiCr}_{0.33}\text{V}_{0.33}\text{Mn}_{0.33}\text{O}_2$  and (b)  $\text{Cu}/\text{LiCr}_{0.33}\text{V}_{0.33}\text{Mn}_{0.33}\text{O}_2$  cathode electrodes.

Figure 4 presents the capacity vs. the cycle number during the first 50 cycles between 3.0 and 4.3 V for  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  and  $\text{Cu}/\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$ . The capacity retention is excellent even for the  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  after the 50 cycles. The capacity retention is 99% for the 1st cycle, it becomes close to 99% in the following cycles. The improvement in capacity may be attributed to the Cr and V content in the lithium plane. This enhances the lithium diffusion in the interslab plane even at relatively high regime. As can be concluded from the Fig. 4, better electrochemical results were obtained. A total capacity retention of 93% was obtained after 50 cycles. A good reversibility of the lithium extraction/insertion was evidenced with very low polarization, given by the difference between charge and discharge curves. This suggests that this sample exhibits low impedance due to the small particle size. Furthermore, the irreversible capacity was quite low indicating good capacity retention of the studied sample [7].

#### 4. Conclusions

In order to optimize the synthesis conditions of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  prepared from the raw mixture obtained by facile sol gel process. It has been revealed that

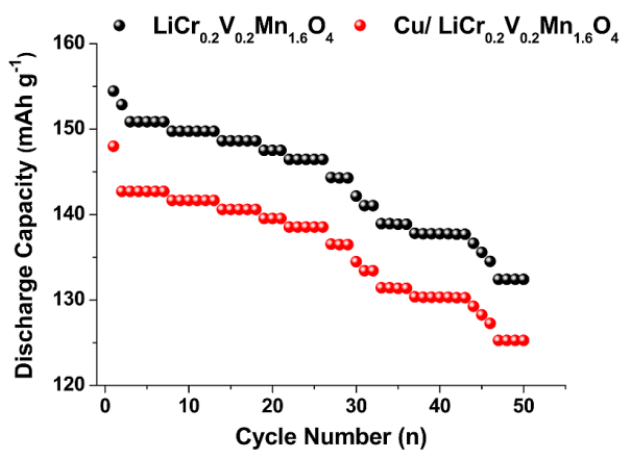


Fig. 4. Discharge capacity vs. cycle number graphs of  $\text{LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  and  $\text{Cu/LiCr}_{0.2}\text{V}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathode electrodes.

this layered compound could be obtained at  $850\text{ }^\circ\text{C}$  for 6 h. In order to increase the electrochemical efficiencies of the as-synthesized electrodes, surfaces of the particles were also coated with copper. Electrochemical tests of the studied cathode, performed in the 3.0–4.3 V window, with 1C current rate, show that the initial discharge capacity was superior as  $158\text{ mA h g}^{-1}$  for surface modified

electrodes. The capacity retention in the case of copper modified electrodes is found to be  $132\text{ mA h g}^{-1}$  after 50 cycles with a capacity retention of 93%. The results have shown that sol-gel processes and electroless coating techniques are efficient and low cost methods in producing high capacity and stable cathode active electrodes.

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