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Aqueous processing of lithium-ion battery cathodes using hydrogen peroxide-treated vapor-grown carbon fibers for improvement of electrochemical properties

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Abstract The electrochemical behavior of aqueous processing lithium cobalt oxide ($LiCoO_2$) cathodes used hydrogen peroxide (H_2O_2)-treated vapor-grown carbon fibers (VGCFs) as a conductive agent for lithium-ion batteries has been investigated and improved. The sedimentation experiments show that the dispersibility in water of H_2O_2-treated VGCFs is better than that of KS-6 (flaky graphite) or as-received VGCFs. This improvement is due to the surface chemistry of H_2O_2-treated VGCFs has become more hydrophilic that was evidenced by its significant shift of iso-electric point (I.E.P) from pH 6.7 to 5.0. As a result, the H_2O_2-treated VGCFs can be well-dispersed in the $LiCoO_2$ electrode which was observed by scanning electron microscope. Furthermore, the rate capability results of electrodes show that addition with H_2O_2-treated VGCFs has better performance than that with KS-6 or as-received VGCFs.

Introduction

Lithium cobalt oxide ($LiCoO_2$) is the most widely used cathode active material in the lithium-ion battery industry due to its high energy density, safety, and good cycling-life performance [1, 2]. The $LiCoO_2$ cathode is generally composed of $LiCoO_2$ powder, conductive additive, and polymer binder [3–6]. These compositions need to be homogeneously mixed into the solvent during the coating process [7–11]. According to the type of solvent used, the processing of electrodes can be classified into two categories—water-based (aqueous) and organic solvent-based (nonaqueous) system [12]. For the consideration of the environment and cost, the water-based system has attracted increasing attention. However, this kind of system has the drawback of powder agglomeration caused by hydrogen bonding and strong electrostatic force [13]. In order to obtain a reliable high-quality electrode, the agglomeration of powders should be strictly avoided. The agglomeration of either the active material or the conductive additive decreases the contact opportunity between them, and then results in a low electrical conductivity of electrodes. The low electrical conductivity will reduce the rate capability of batteries. Therefore, it is essential to obtain a well-dispersed powder suspension during the manufacturing process of electrodes.

Owing to the superior electrical, thermal, and mechanical properties of carbon nanofibers, many potential applications have been proposed. For example, vapor-grown carbon fibers (VGCFs) have been used as conductive agents in nonaqueous-processed $LiCoO_2$ cathodes to improve the electrochemical properties of aqueous processed cathodes of lithium-ion batteries [14–17]. The fibroid VGCFs are expected to behave like electron-conducting bridges between adjacent active cathode/anode particles, which can

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facilitate the electron transfer. However, most as-received VGCFs are olephilic and only appropriate for use in the organic-based cathode processes. Therefore, the aggregation of VGCFs is significant in aqueous suspensions because the olephilic fibers are difficult to wet and disperse in water. In order to obtain a well-dispersed slurry, the surface treatment of VGCFs is required.

Until now, the only effective approach for dispersing carbon materials such as carbon nanotubes and nanofibers in water was the chemical treatment by refluxing carbon materials in concentrated acids [18–22], such as sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), or the mixtures of these acids. Although this approach can greatly increase the dispersion properties, the length and the π–π conjugated structure of carbon nanotubes and nanofibers will be significantly distorted due to the vigorous acid attack, which result in diminished mechanical and electrical properties [23, 24]. Moreover, residual acids were found to be adsorbed by the large-area fibers and are difficult to remove from the surface of fibers. Therefore, the above drawbacks of acid treatments will limit their potential applications [25]. In addition, a great deal of waste of concentrated acids is another environmental problem. In order to avoid the above-mentioned drawbacks, some literature reported a milder method to modify the surface of carbon materials by using oxidation with hydrogen peroxide (H_2O_2) solution [25–29].

In this article, we added treated VGCFs that well disperse in aqueous system for water-based processing cathodes to increase the electrical conductivity of electrodes to improve the rate capability of the lithium-ion battery. The VGCFs were treated by a milder method using H_2O_2 to modify their surface. The effect of the H_2O_2-treated VGCFs as a conductive agent on the dispersion and electrochemical properties of $LiCoO_2$ cathodes was studied and compared to the results of conductive additives of pure KS-6 graphite and as-received VGCFs. XPS characterization was used to characterize the chemical composition of the surface of VGCFs. Sedimentation experiments and zeta potential measurements were carried out to explore the dispersion behavior of conductive agents in aqueous suspensions. The dispersion homogeneity of as-prepared $LiCoO_2$ electrode sheets with different conductive agents was analyzed by SEM. The electrical conductivity and rate capability were studied to clarify the influence of surface chemistry and the morphology of conductive agents on the cell performance of $LiCoO_2$ cathodes.

Experimental

The active material of the cathodes used in this study was a high-purity $LiCoO_2$ powder (L106, LICO, Taiwan). The powder had a median size of 8.0 μm with a standard deviation of 0.45 μm measured by the light scattering (LS-230, Coulter Counter, USA) method. The conductive agents used include the synthetic graphite (KS-6, Timcal AG, Sins, Switzerland), VGCFs (VGCF®-H, Showa Denko, Japan), and surface-modified VGCFs. The surface-modified VGCFs were obtained by refluxing the as-received VGCFs in the H_2O_2 solution at 108 °C for 10 h. The binder used was a mixture of SBR (styrene butadiene rubber, Asahi Kasei Corporation, Japan) and SCMC (sodium carboxymethyl cellulose, Aldrich, USA) in a 3:2 ration by weight. The SBR was in the form of an aqueous emulsion of 48 wt.% with a viscosity of 130 mPa s at 25 °C, and the SCMC was a thickening agent with an average molecular weight of 250,000 g/mol and substitution degree (DS) of 1.2. De-ionized water was used as the solvent in this study.

The surface chemistries of KS-6 graphite, as-received VGCFs, and H_2O_2-treated VGCFs were characterized by X-ray photon spectroscopy (XPS) (PHI Quantera SXM, ULVAC-PHI, Inc., Japan) and the technique known as the Electroacoustic method (ZetaProbe, Colloidal Dynamics Inc., USA).

The $LiCoO_2$ electrode sheets were fabricated through a water-based process. Aqueous slurries with 64.75 g (68.0 wt.%) $LiCoO_2$ powder was prepared by mixing additives of 1.05 g (1.6 wt.%) binder and 4.20 g (6.0 wt.%) conductive agent. Three compositions of conductive agents of 6.0 wt.% KS-6, 2.0 wt.% as-received VGCFs + 4.0 wt.% KS-6, and 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6 were used. Note that the contents of all additives were based upon $LiCoO_2$ powder. The slurries were de-agglomerated and mixed by ball milling with Y_2O_3-stabilized ZrO_2 media for 48 h at room temperature and the pH values were controlled at 9.5 by an aqueous solution of oxalic acid ($H_2C_2O_{4\ (aq)}$). The as-prepared slurries were then cast on one side of a piece of aluminum (Al) foil by using a comma coater and passed through a baking oven at the temperature of 130–140 °C to be dried. The final thickness of the $LiCoO_2$ sheets after drying and pressing were approximately 85 μm and 65 μm, respectively.

The microstructures of the dried sheets were examined by a field emission scanning electron microscope (FESEM, S-4000, Hitachi). The $LiCoO_2$ electrode sheets were further dried in a vacuum oven at the temperature of 100 °C for 6 h in order to decrease the moisture to 20–40 ppm, and then the surface resistance was measured by a two-point resistance test using a MCP-TESTER FP analyzer.

The electrochemical performance was evaluated by assembling cathode-limited 2016 lithium coin cells. $LiCoO_2$ was used as the cathode and the lithium metal foil was used as the anode. A separator (Celgard 2320) was placed between the cathode and the anode. The electrolyte was 1.0 M lithium hexafluorophoshate ($LiPF_6$, Ferro, USA) in EC:PC:DEC (3:2:5 in volume) mixed solvents. The cells were charged at a constant current at 0.2 C to 4.2 V and discharged at 0.2, 1, and 3 C to 2.75 V. Note that all of the above processes were carried out in a dry room (dew point = –45 °C).

Results and discussion

The dispersibility of conductive agents in water

The dispersibility of 0.1 wt.% of KS-6 graphite, as-received VGCFs, and H_2O_2-treated VGCFs in water was determined by observing their sedimentation behaviors in water after 3 days as shown in Fig. 1a, b, and c, respectively. Figure 1a shows that the KS-6 powder easily settles down to the bottom of the vial. This result indicates that KS-6 has a poor dispersion in water although it can be wetted in water. For the as-received VGCFs (Fig. 1b), most of VGCFs precipitate to the bottom and some of VGCFs float on the water. This result indicates that the as-received VGCFs are very poor to be wetted and dispersed in water. Moreover, the high sedimentation volume indicates that the as-received VGCFs were heavily aggregated and thus loosely packed. However, the H_2O_2-treated VGCFs were well dispersed in water (Fig. 1c). This improvement is due to the fact that the milder oxidative condition by H_2O_2 can introduce hydrophilic groups like hydroxyl (–OH), carboxyl (–COOH), or carbonyl (–C(=O)) groups on the defect sites of carbon nanofibers [13–15]. Therefore, the wetting and dispersion property of the H_2O_2-treated VGCFs can be significantly improved.

The surface chemistry of conductive agents

According to the good wettability of H_2O_2-treated VGCFs in water, the oxygen-containing group should be polar functional groups. In order to clarify the effect of H_2O_2 treatment on the surface chemistry, the as-received VGCFs and H_2O_2-treated VGCFs were characterized by XPS as shown in Fig. 2. The Fig. 2a presents the as-received VGCFs have a very weak oxygen peak about 2.5 atom%. Figure 2b shows that an obvious increase in oxygen content was observed from 2.5 to 3.4 atom% after the H_2O_2-treatment. This result indicates that the surface of H_2O_2-treated VGCFs forms new oxygen-containing functional groups. Furthermore, the O 1s peaks of H_2O_2-treated VGCFs in Fig. 2b show two peaks. The lower-energy peak is assigned to the $O{-}C{=}\underline{O}$ or $C{=}\underline{O}$ at 531.9 eV. The high-energy peak is attributed to $\underline{O}{-}C = O$, $C{-}\underline{O}H$, or $H_2\underline{O}$ at 533.2 eV [30, 31]. Obviously, the XPS results also indicate that the surface of H_2O_2-treated VGCFs should be polar functional groups, such as hydroxyl (–OH), carboxyl (–COOH), or carbonyl (–C(=O)) groups.

The surface chemistry of VGCFs was also identified by analysis of zeta-potential as shown in Fig. 3. Figure 3a shows that the iso-electric point (I.E.P) of as-received VGCFs is pH 6.7. This result indicates that the surface of the as-received VGCFs is almost neutral because they were graphitized. After the graphitization, most heteroatoms on the surface almost were eliminated. Figure 3b shows that the iso-electric point (I.E.P) of H_2O_2-treated VGCFs shifted from pH 6.7 to 5 after the H_2O_2-treatment. The I.E.P. shift indicates that the surface chemistry of VGCFs has been altered and becomes more acidic because the surface of VGCFs is oxidized by H_2O_2 to form more acidic functional groups such as hydroxyl, carboxyl, or carbonyl

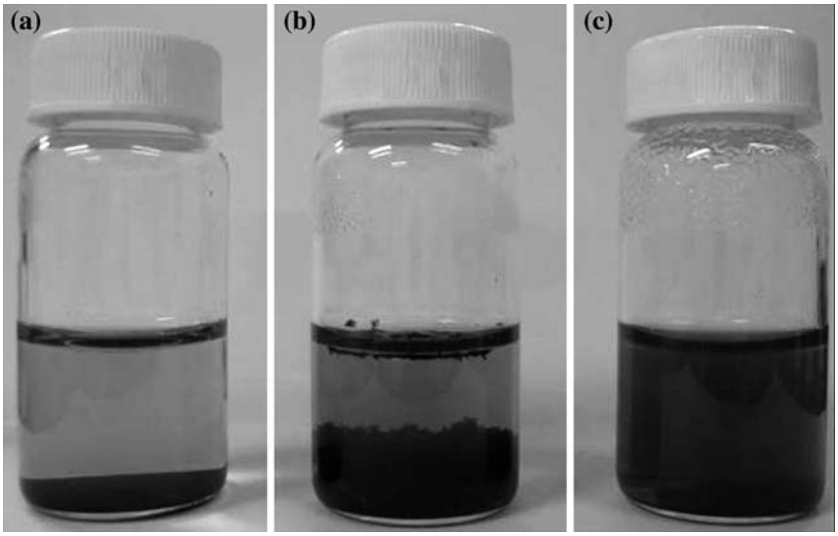

Fig. 1 Sedimentation pictures of 0.1 wt.% (a) KS-6 graphite, (b) as-received VGCFs, and (c) H_2O_2-treated VGCFs in water after 3 days

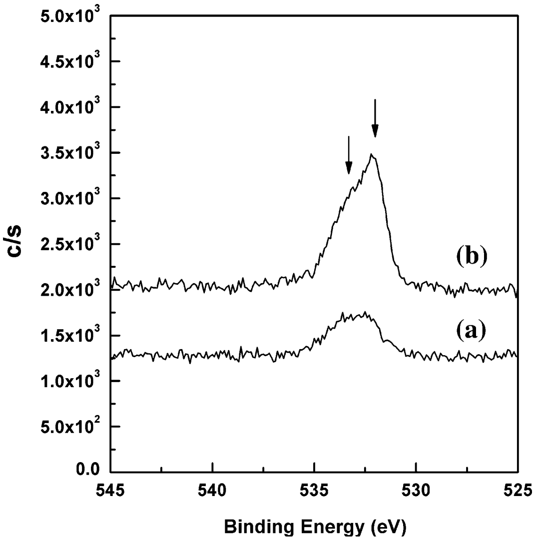

Fig. 2 O 1s region of X-ray photon spectra for (a) as-received VGCFs and (b) H_2O_2-treated VGCFs

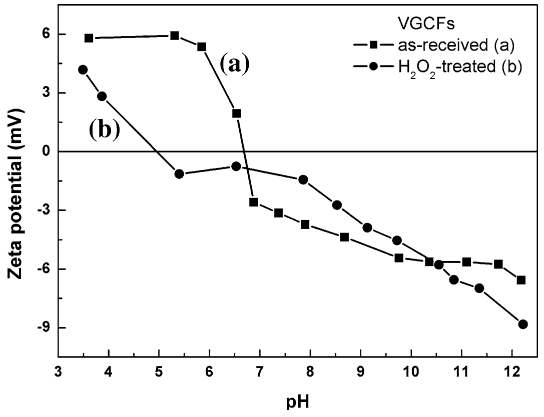

Fig. 3 Zeta potentials of 1 wt.% (a) as-received and (b) H_2O_2-treated VGCFs in water

groups. In the previous report, we also found the similar result in multi-layered carbon nanotubes [25]. After the milder oxidative treatment, the functional groups of the VGCFs' surface are changed. Therefore, the wetting and dispersion property of H_2O_2-treated VGCFs would be better than that of as-received VGCFs.

The microstructures of $LiCoO_2$ electrodes

Figure 4a, b, and c show the SEM micrographs for the top-viewed microstructures of $LiCoO_2$ electrode sheets with additions of the conductive agents 6.0 wt.% KS-6, 2.0 wt.% as-received VGCFs + 4.0 wt.% KS-6, and 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6, respectively. Components are labeled in all the figures for easy identification. From Fig. 4a, it can be seen that the KS-6

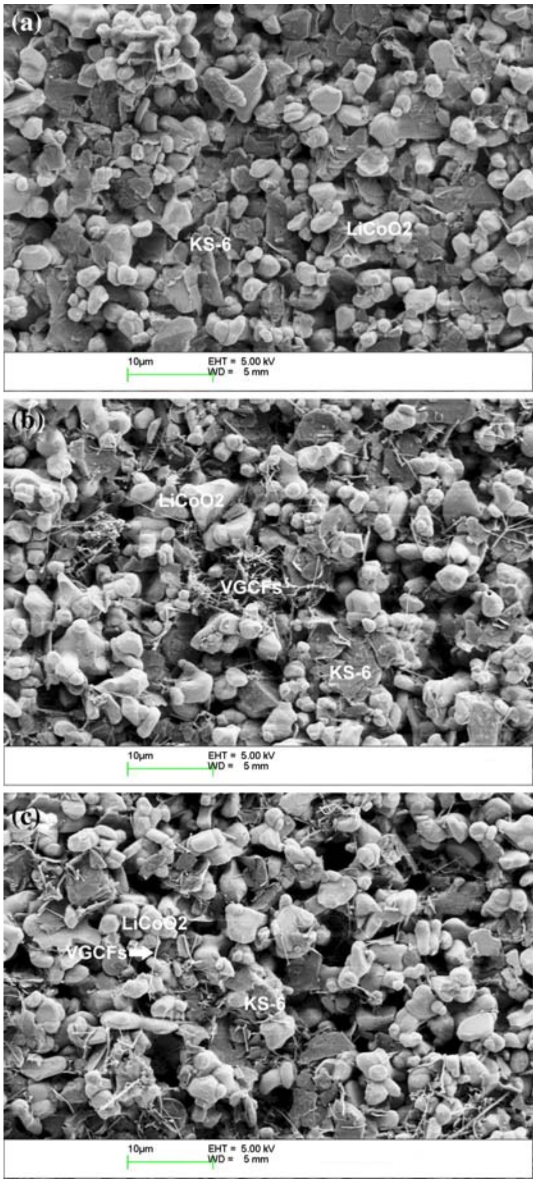

Fig. 4 SEM micrographs of top-viewed $LiCoO_2$ electrode sheet with respective addition of conductive agent of (**a**) 6.0 wt.% KS-6 graphite, (**b**) 2.0 wt.% as-received VGCFs + 4.0 wt.% KS-6 graphite, and (**c**) 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6

graphite is almost homogeneously distributed among the $LiCoO_2$ particles. When one-third of the KS-6 graphite amount was replaced by as-received VGCFs, the KS-6 graphite can still remain well distribute but the as-received VGCFs are significantly aggregated (Fig. 4b). Also, most of the aggregated VGCFs are confined to the site of the graphite, and this aggregation decreases its contact opportunities with $LiCoO_2$ particles. Thus, it would be difficult to improve the electrical translation between the active material and the conductive agents for the electrode with addition of the as-received VGCFs. Comparing

Fig. 4b and c obviously shows the H_2O_2-treated VGCFs are more homogeneously distributed and there are fewer aggregates. Therefore, the H_2O_2-treated VGCFs can behave as a bridge between the active powders to build a three-dimensional connected network structure inside the electrode sheet to efficiently conduct electrons [1, 4], which would facilitate the cell performance of cathodes.

The electrical conduction of $LiCoO_2$ electrodes

To further understand the effect of the addition of carbon fibers on the electrical conduction of $LiCoO_2$ electrode sheets, the surface resistance of the sheets with respective addition of the above three conductive agents was measured. The obtained electrical conductivity of electrodes with 6.0 wt.% KS-6 graphite, 2 wt.% as-received VGCFs + 4.0 wt.% KS-6, and 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6 before pressing treatment is 414, 212, and 195 ohm cm, respectively. In order to enhance the adhesion and electrical conductivity of electrodes, the electrodes were pressed to 80% by a roller. After pressing treatment, the electrical conductivity of electrodes with 6.0 wt.% KS-6 graphite, 2 wt.% as-received VGCFs + 4.0 wt.% KS-6, and 2% H_2O_2-treated VGCFs + 4.0 wt.% KS-6 is 151, 208, and 125 ohm cm, respectively. From the above results, it can be found that the sheet with the addition of pure KS-6 graphite has the highest resistance before pressing. This result represents that VGCFs as conductive agents are more efficient in conducting electrons, which may be due to their lower electrical resistivity (10^{-4} ohm cm) than that of graphite (10^{-3} to 10^{-2} ohm cm) [1] or their special physical morphology that can form a three-dimensional conducting network. Interestingly, the electrical resistances of the sheet with the addition of pure KS-6 and the sheet with the addition of 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6 are both significantly decreased from 414 to 151 ohm cm and 195–125 ohm cm after pressing, respectively. This result illustrates that the KS-6 graphite and H_2O_2-treated VGCFs are just weakly aggregated and hence both are easy to shear and be dispersed during the pressing process, resulting in a decreased surface resistance. However, for the sheet with the addition of 2.0 wt.% as-received VGCFs + 4.0 wt.% KS-6, the electrical resistance almost remains unchanged about 210 ohm cm. This gives evidence of strong aggregation between fibers, which are not easily sheared apart. Therefore, in order to make the VGCFs an efficient conductive additive, surface treatment is required; otherwise, the originally poor dispersion and wetting properties would countervail its conformational advantage for conducting electrons.

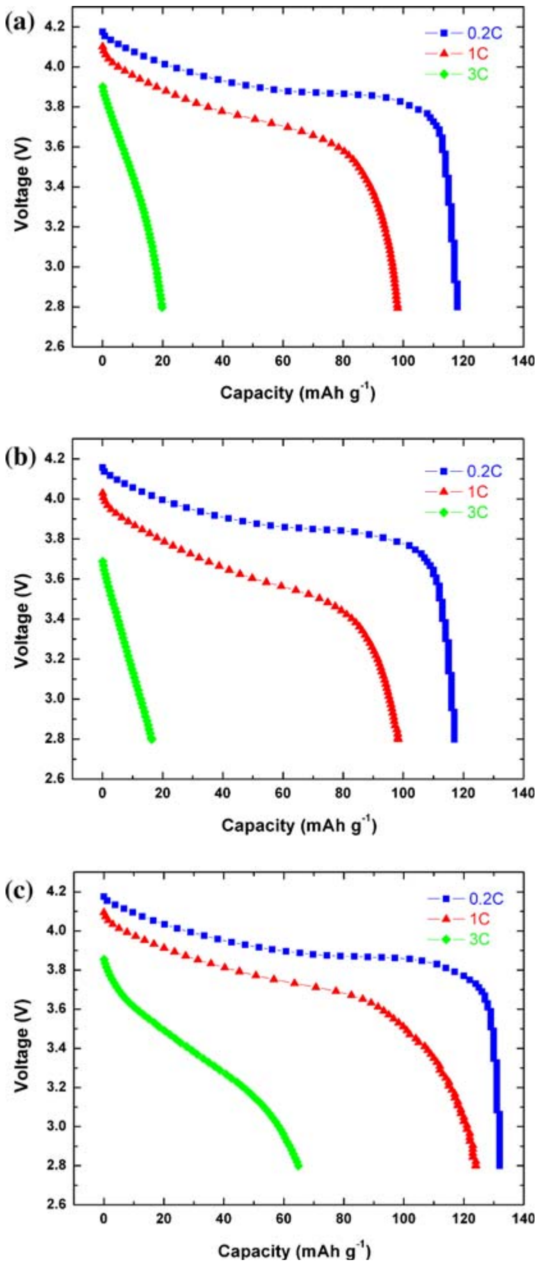

Fig. 5 Discharge curves at various discharge rates for $LiCoO_2$/Li half-cells prepared with the addition of different conductive agents of (**a**) 6.0 wt.% KS-6 graphite, (**b**) 2.0 wt.% as-received VGCFs + 4.0 wt.% KS-6 graphite, and (**c**) 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6 graphite

The electrochemical property of $LiCoO_2$ electrodes

To clarify the effect of the addition of carbon fibers on the electrochemical properties of $LiCoO_2$ cathodes, the C-rate performance of $LiCoO_2$ electrodes with 6.0 wt.% KS-6 graphite, 2.0 wt.% as-received VGCFs + 4.0 wt.% KS-6, and 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6 at 0.2, 1, and 3 C was then measured as shown in Fig. 5a–c, respectively. The results show that the rate capability of the cell with the conductive agent of as-received VGCFs is approximately that of KS-6 graphite. No positive effect on improving the electrical conductivity and rate capability was obtained. According to the prior dispersion data, the as-received VGCFs are hydrophobic and aggregate (Fig. 4b); replacing 2 wt.% KS-6 amount with as-received VGCFs is ineffectual. Instead, a significant improvement of C-rate performance was observed for the cell with the addition of the conductive agent, 2.0 wt.% H_2O_2-treated VGCFs + 4.0 wt.% KS-6, as shown in Fig. 5c. Therefore, to improve the electrochemical property of water-based cathodes, the added VGCFs need to be deflocculated and dispersed by an appropriate surface treatment, such as oxidation by H_2O_2.

Conclusions

The effects of adding a fibroid conductive agent, VGCFs, on the dispersion behavior of aqueous $LiCoO_2$ slurries and their corresponding cell performances have been investigated. The as-received VGCFs are hydrophobic and form hard aggregates that cause difficulty with wetting or dispersion in an aqueous $LiCoO_2$ slurry; therefore, its as-prepared cathode has no improved performance on the electrical resistance and C-rate capability. When the VGCFs were treated with the H_2O_2 solution, they become hydrophilic and softly agglomerated, which made them easily dispersed during the aqueous process. The dispersed fibroid VGCFs in the as-prepared electrode sheet are just like a three-dimensional network that can efficiently conduct electrons. Thus, the added VGCFs should be pretreated in order to obtain their morphological advantage, i.e., good dispersion that aids in improving electrical conductivity; pretreatment by a milder oxidation with H_2O_2 is an appropriate methodology.

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References

1. Dey AN, Sulliva BP (1970) J Electrochem Soc 117:222
2. Wolverton C, Zunger A (1998) J Electrochem Soc 145:2424
3. Cheon SE, Kwon CW, Kim DB, Hong SJ, Kim HT, Kim SW (2000) Electrochim Acta 46:599
4. Fransson L, Eriksson T, Edström K, Gustafsson T, Thomas JO (2001) J Power Sources 101:1
5. Liu Z, Yu A, Lee JY (1998) J Power Sources 74:228
6. Kim KM, Jeon WS, Chung IJ, Chang SH (1999) J Power Sources 83:108
7. Kosova N, Devyatkina E, Osintsey D (2004) J Mater Sci 39:5031
8. Kim J, Kim B, Lee JG, Cho J, Park B (2005) J Power Sources 139:289
9. Li CC, Lee JT, Lo CY, Wu MS (2005) Electrochem Solid State Lett 8:A509
10. Li CC, Lee JT, Peng XW (2006) J Electrochem Soc 153:A809
11. Yang HQ, Li DP, Han S, Li N, Lin BX (1995) J Power Sources 58:221
12. Saekil S, Lee J, Zhang Q, Saito F (2004) Int J Miner Process 74S:S373
13. Nahass P, Rhine WE, Pober RL, Bowen HK, Robbins WL (1990) In: Nair KM, Pohanka R, Buchanan RC (eds) Ceramic transactions, vol 15. American Ceramic Society, Westerville, p 355
14. Endo M, Kim YA, Takeda T, Hong SH, Matusita T, Hayashi T, Dresselhaus MS (2001) Carbon 39:1287
15. Mizuno F, Hayashi A, Tadanaga K, Tatsumisago M (2005) J Electrochem Soc 152:A1499
16. Mizuno F, Hayashi A, Tadanaga K, Tatsumisago M (2005) J Power Sources 146:711
17. Her LJ, Hong JL, Chang CC (2006) J Power Sources 157:457
18. Liu J, Rinzler AG, Dai HJ, Hafner JH, Bradley RK, Boul PJ, Lu A, Iverson T, Shelimov K, Huffman CB, Rodriguez-Macias F, Shon YS, Lee TR, Colbert DT, Smalley RE (1998) Science 280:1253
19. Jia Z, Wang Z, Liang J, Wei B, Wu D (1999) Carbon 37:903
20. Saito T, Matsushige K, Tanaka K (2002) Physica B 323:280
21. Wang Y, Wu J, Wei F (2003) Carbon 41:2939
22. Hilding J, Grulke EA, Zhang ZG, Lockwood F (2003) J Disper Sci Technol 24:1
23. Hirsch A (2002) Angew Chem Int Ed 41:1853
24. Hamon MA, Chen J, Hu H, Chen Y, Itkis ME, Rao AM, Eklund PC, Haddon RC (1999) Adv Mater 11:834
25. Li CC, Lin JL, Huang SJ, Lee JT, Chen CH (2007) Colloids Surf A 297:275
26. Goto H, Furuta T, Fujiwara Y, Ohashi T (2003) US patent 20030007924A1
27. Hernadi K, Siska A, Thien-Nga L, Forrob L, Kiricsi I (2001) Solid State Ionics 141:203
28. Gil A, de la Puente G, Grange P (1997) Microporous Mater 12:51
29. Concheso A, Santamaría R, Menéndez R, Jiménez-Mateos JM, Alcántara R, Lavela P, Tirado JL (2006) Electrochim Acta 52:1281
30. Xing Y, Li L, Chusuei CC, Hull RV (2005) Langmuir 21:4185
31. Hontora-Lucas C, Lopez-Peinado AJ, Lopez-Gonzales JD, Rojas-Cervantes ML, Martin-Aranda RM (1995) Carbon 33:1585