Dynamic Observation of Reversible Lithium Storage Phenomenon in Co₃O₄/CNTs Hybrid Devices

Guan-Min Huang¹, Tsung-Chun Tsai¹, Chun-Wei Huang¹, and Wen-Wei Wu¹

¹ National Chiao Tung Univ.

Department of Materials Science and Engineering No.1001, University Rd., East Dist., Hsinchu City 30010, Taiwan. Phone: +886-3-5712121-55395 E-mail: wwwu@mail.nctu.edu.tw

Abstract

Carbonaceous composites have attracted much attention as anode materials for hybrid supercapacitors. Additionally, transition metal oxides, such as Co₃O₄, have high specific capacitance in the charging/discharging process. Here, we investigated the lithium storage mechanism of Co₃O₄/CNTs material via in situ transmission electron microscopy (TEM). Additionally, we analyzed the structure and composition of the anode material by high-resolution TEM, electron diffraction, energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Using our unique in situ experimental setup that employs colloidal electrolyte, we elucidate two different mechanisms during operation, including the phase evolution and volume variation of the electrode material. Our observations not only provide direct evidence of the electrochemical behavior but also improve the structure to promote enhanced performance for the application of hybrid supercapacitors.

1. Introduction

As the ever-growing demand for high-capacity electrical energy storage increases, novel energy storage systems should be developed for diverse applications. Among these, supercapacitors and batteries have received an increased amount of attention in recent years ^[1,2]. Supercapacitors have unique characteristics of high power density and rapid charge time, whereas batteries function by a redox reaction on the electrode materials and provide distinguishing feature of high energy density. Recently, to advance their applicability on electronics, hybrid supercapacitor was developed to become a rising star system with the integration of the advantages from supercapacitors and batteries ^[3-5].

For energy storage systems, selecting an appropriate electrode material is one of the major factors influencing the electrical performance ^[6,7]. It is widely known that transition metal oxides have extremely high specific capacitance due to their multiple oxidation states. They are great candidates to develop an exceptional energy storage system. Nevertheless, there are still some difficulties to overcome; for example, their poor electron conductivity restricts their development in devices. Thus, for these reasons, carbonaceous materials, such as CNTs and graphene, have been integrated with transition metal oxides to synthesize "composite materials" to combine the advantages of both materials and achieve improved properties. In this study, we prepare a composite electrode material comprised of Co_3O_4 and CNTs to reveal the correlation between the electrochemical reaction and the structural evolution. For this purpose, we designed a nano hybrid supercapacitor for transmission electron microscope (TEM) observation to examine the lithium storage mechanism of the Co_3O_4 /CNTs material. In situ TEM has become a powerful technique to provide the real-time investigation of device operation^[8,9]. With this technique, we can discern the full mechanism regarding the charging/discharging process to understand ion transport behaviors and enhance the performance through structural modification.

2. Method, Results and Discussion

Here, we constructed an electrochemical device for in situ TEM observation to reveal the charging/discharging behavior of hybrid supercapacitor. The detailed schematic illustration of our experimental setup composed of a $Co_3O_4/CNTs$ electrodes and LiPF₆ electrolyte is shown in Fig. 1a. A potential of -5 V with respect to the cathode was applied to the $Co_3O_4/CNTs$ anode during the charging process. Figures 1b-e display the time-lapse images captured from in situ TEM video, showing the structural evolution over the charging duration. We can clearly observe that several cube-like Co_3O_4 particles combined to transform into numerous nanograins after charging for 60 s. To acquire a thorough structural and phase characterization, the technique of high-resolution TEM



Fig. 1. TEM images showing the structural evolution and volume expansion during charging at -5 V against the cathode.



Fig. 2. Time-lapse structural evolution and phase transformation during discharging at +5 V against the cathode.

and EELS identified that Co nanograins dispersed in the matrix, as displayed in Fig. 1f and g. Therefore, the reaction behavior is concisely expressed in the schematic illustration shown in Fig. 1h. The drawing demonstrates the correlation between the reaction front and the mode of energy storage. Remarkably, this type of near-surface redox reaction may exhibit supercapacitor-like behavior ^[10].

To obtain a more complete operation mechanism, inspection of the discharging behavior is necessary. The in situ observation upon applying +5 V against the cathode to the device can be seen in Fig. 2a-d. The Co nanograins tend to gather and form lager particles in the matrix upon discharging over time but the shape of the Li₂O matrix almost remained the same. The morphological change that these Co nanograins underwent in the transformation to CoO particles, which were examined by the diffraction pattern from FFT (Fig. 2e) and the EELS (Fig. 2f), was clearly observed. Moreover, in Fig. 2g and i, it is easy to distinguish the apparent difference in morphology before and after the discharging process. After discharging, as shown in Fig. 2j, the size of the Co or CoO clusters (marked by red dashed lines) inside the Li₂O matrix decreased from 45.5 nm to 31.5 nm, an approximately -66.8% volume variation relative to that before discharging, as presented in Fig. 2h. Noticeably, with regards to the Co₃O₄/CNTs system, the conservation of SEI enhances the stability and prolongs the life cycle.

Using the finding mentioned above, the schematic drawing shown in Fig. 3 expresses the complete operation mechanism in our Co₃O₄/CNTs system. First, in the first charging cycle, the Li ions intercalate and flow *via* the interlayer spacing of CNTs, and the electrochemical reaction can be revealed to be $Co_3O_4 + 8Li^+ + 8e^- \rightarrow 3Co + 4Li_2O$. Afterwards, once the first charging cycle is finished, the phase transformation is followed by the reversible reaction $Co + Li_2O \leftrightarrow$ $CoO + 2Li^+ + 2e^-$. With the mechanism that we revealed, this variation in the first charge cycle may be regarded as the major factor influencing the performance.



Fig. 3. Schematic drawing of the charging and discharging mechanisms in the $Co_3O_4/CNTs$ system.

3. Conclusions

We have revealed the overall mechanism for charging and discharging. Our experiment closely resembles the actual operation of real hybrid supercapacitors. Consequently, with the aid of in situ TEM observations, our experimental setup can provide more direct and compelling evidence to study the electrochemical behavior of $Co_3O_4/CNTs$. In summary, the near-surface redox reaction and ions intercalation phenomenon in CNTs presented hybrid supercapacitor-like behavior. The electrochemical reaction become nearly reversible as long as this device experienced first charging. Furthermore, the results will undoubtedly be useful for improving the structure to promote better performance for the application of hybrid supercapacitors.

Acknowledgements

The authors acknowledge the support by the Ministry of Science and Technology through Grants 103-2221-E-009-222-MY3, 104-2221-E-009-050-MY4, and 105-3113-E-009-002.

References

- [1] P. Simon and Y. Gogotsi: Nat Mater. 7 (2008)845.
- [2] P. Simon, Y. Gogotsi and B. Dunn: Science. 343 (2014)1210.
- [3] M.R. Lukatskaya, B. Dunn and Y. Gogotsi: Nature Communications. 7 (2016)12647.
- [4] E. Lim, C. Jo, M.S. Kim, M.-H. Kim, J. Chun, H. Kim, J. Park, K.C. Roh, K. Kang, S. Yoon and J. Lee: Advanced Functional Materials. 26 (2016)3711.
- [5] C. Himani, K.S. Manoj, K. Praveen, H. Safir Ahmad and D. Sasanka: Nanotechnology. 28 (2017)025401.
- [6] C.J. Hung, J.H. Hung, P. Lin and T.Y. Tseng: Journal of The Electrochemical Society. 158 (2011)A942.
- [7] N. Kumar, C.-W. Huang, P.-J. Yen, W.-W. Wu, K.-H. Wei and T.Y. Tseng: RSC Advances. 6 (2016)60578.
- [8] K.-C. Chen, W.-W. Wu, C.-N. Liao, L.-J. Chen and K.N. Tu: Science. 321 (2008)1066.
- [9] J.-Y. Chen, C.-W. Huang, C.-H. Chiu, Y.-T. Huang and W.-W. Wu: Advanced Materials. 27 (2015)5028.
- [10] K. He, H.L. Xin, K. Zhao, X. Yu, D. Nordlund, T.-C. Weng, J. Li, Y. Jiang, C.A. Cadigan, R.M. Richards, M.M. Doeff, X.-Q. Yang, E.A. Stach, J. Li, F. Lin and D. Su: Nano Letters. 15 (2015)1437.