Lithium batteries are key energy storage devices that have attracted great attention for use in portable devices and electronic vehicles. At present, most of the cathode materials used for lithium batteries are based on lithium intercalation compounds, such as lithium transition-metal oxides (LiCoO₂, LiMn₂O₄, etc.), or polyanion-based compounds (LiFePO₄, LiFeSiO₄, etc.). The capacity and cycle performance of these cathode materials are limited mainly by the reversibility of the crystal structures during the extraction-insertion of lithium located in the lattice structures, as was discussed in our previous papers. Once the lithium is extracted over the reversibility limit of crystal structure, the cathode materials lose cycle stability and battery performance deteriorates drastically.

We propose that polyoxometalates (POMs), which are molecular cluster-ion materials, can be used as high-capacity cathode materials in lithium batteries on the basis of the multi-electron redox reaction. POMs have individual molecular clusters and good cycle stability; this is because the capacity and cycle stability of molecular cluster-ion materials are independent from the stability of its crystal structure. An initial discharge capacity of over 400 mAhg⁻¹ was reported for POMs. In addition, POMs can be synthesized by self-assembly, especially in polyanion-based compounds like LiFePO₄. Lithium batteries using POMs as a solid catalyst is known to be very high. In a previous paper, we reported on sub-reactions on the surface of various kinds of POMs. In addition, this surface reaction was reported to impair the cycle stability of the battery.

Polyoxometalates have been investigated for use as high-capacity cathode materials in lithium batteries due to their high capacity, cycle stability, and recoverability of crystal structure during charge-discharge. However, POMs have weak points when used as the cathode electrode for lithium batteries: low electronic conductivity and high surface reactivity. In this study, we used a conducting polymer, polypyrrole (PP), to coat the surface of nano-sized polyoxovanadate K₉PV₁₄O₃₂ (KPV) and examined the electrochemical properties. By optimizing the coating conditions, the PP uniformly covers the surface of KPV nanoparticles, with a thickness of about 5 nm. The capacity of PP-coated KPV increased to 500 mAhg⁻¹ and 90% of its initial capacity was retained after 50 cycles. The capacity at high current density (1000 mAhg⁻¹) was also improved from 200 mAhg⁻¹ to 280 mAhg⁻¹, with 93% capacity retention after 50 cycles. This high capacity and rate performance is due to the improvement in the electronic conductivity of POMs. The PP layer also suppressed the surface reactions in KPV, which improves the cycle stability of the cell.

In order to overcome these disadvantages of POMs for use as cathode materials, we coated the surface of nano-sized POM particles with a conducting polymer. This is expected to increase electron transport to the POM particles and suppress the surface reactions on the surface of POMs. In this paper, we used a conducting polymer, polypyrrole (PP), to coat nano-sized polyoxovanadate K₉PV₁₄O₃₂ (KPV) and examined its electrochemical properties.

**Experimental**

The synthesis of KPV is reported in our previous paper. In order to prepare nano-sized particles, 0.2 g of as-prepared KPV powders were dissolved in 10 ml of distilled water. The precipitated particles were obtained by adding 50 ml of a water-soluble solvent, acetone, to the aqueous solution, followed by centrifugation and washing with acetone. To remove the water contained in the powders, both as-prepared and precipitated products were dried at 120 °C under air for 1 h. The weight of polymer on the cathode material was not collected.

The identification of the products was carried out by XRD measurements using a powder X-ray diffractometer (Rigaku RAD-C) with Cu Kα radiation. The morphology of the powder samples was observed by a scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEOL JSM 2250). The electrochemical performance of the cells was studied by discharge-charge cycle tests and AC-impedance measurements at 25 °C. The cathode consists of 30 wt% active material, 65 wt% Ketjen Black (KB), and 5 wt% PTFE binder. An ethylene carbonate-diethyl carbonate mixed solvent (3:7) with a supporting electrolyte of 1 M LiPF₆ (Kishida battery grade) and lithium metal (Honjyo Metal) were used as the electrolyte and anode material, respectively. The discharge-charge characteristics of the samples were examined using a CR-2032 coin cell with a battery tester (Interface model 020-A19). AC-impedance spectra for cells were obtained using a frequency-response analyzer (Solatron 1255) connected to a potentiostat (Solatron 1280) in the frequency range of 10⁻² to 10⁶ Hz with an applied potential of 0.02 V from the cell voltage.

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Results and Discussion

The XRD patterns of as prepared and re-precipitated KPV are shown in Figure 1. Both patterns agree with the results in our previous report and it is clear that the crystal structure of KPV is not affected by the re-precipitation. The peak intensity of nano-sized KPV (n-KPV) decreased, which could be caused by the decrease in crystallinity of KPV.

In Figure 2, SEM images of as prepared KPV (a) and KPV after re-precipitation (b) are shown. The particle shape of KPV drastically changed from having a heterogeneous structure, with sizes in the range of 2–10 μm, to having a uniform structure with sizes in the range of 200–500 nm after re-precipitation; the crystal morphology also changed from heterogeneous to uniform cubic. This downsizing effect is inherent to molecular compounds.

The electrochemical property of n-KPV was examined by constant current charge-discharge tests. The charge-discharge curves for micro-sized KPV (m-KPV) and n-KPV are shown in Figures 3a and 3b, respectively. The maximum discharge capacity of n-KPV was improved, with a value of 520 mAh g\(^{-1}\) (in the third cycle) at a current density of 16 mAh g\(^{-1}\), compared with m-KPV, with a value of 220 mAh g\(^{-1}\) in the first cycle and 250 mAh g\(^{-1}\) in the second cycle. In a previous paper, we reported that the maximum capacity of micro-sized KPV is 220 mAh g\(^{-1}\). In the present paper, the initial discharge capacity is improved to 250 mAh g\(^{-1}\) even for the micro-sized sample. This increase in the discharge capacity could be caused by changing the conductive carbon additive from Acetylene Black (AB) to Ketjen Black (KB), which has a much higher electronic conductivity and surface area. This increase of capacity induced by the additive with high conductivity suggests that the low electronic conductivity of POM inhibits its inherent capacity. In a previous study, we reported that the capacity of an Anderson-type POM, Na\(_3\)[AlMo\(_6\)O\(_{24}\)H\(_6\)], could be improved by mixing the active materials with a conductive additive, KB, homogeneously using a satellite ball mill. LiFePO\(_4\), which has an olivine-type structure, is a famous cathode material for lithium batteries with low electronic conductivity. To improve the inherent capacity, it is reported that mixing downsized particles of the cathode material (to the nano-scale) with the conductive additives is effective.

In Figure 3c, the cycle stability results of m-KPV and n-KPV are shown. The micro-sized KPV shows a stable cycle stability with a capacity retention of 95% after 50 cycles, whereas the capacity of nano-sized KPV decreased gradually and the capacity retention after 50 cycles was 72%. This capacity decrease of n-KPV seems to...
be caused by the surface sub-reactions such as the decomposition of the electrolyte and surface film formation,\textsuperscript{31,13} POMs originally have a strong catalytic activity as acid catalysts\textsuperscript{24} and downsizing POM particles will enhance this activity. In our previous work, we identified the by-products on the surface of an Anderson-type POM, Na\textsubscript{8}[AlMo\textsubscript{6}O\textsubscript{17}H\textsubscript{4}], such as LiF and Li\textsubscript{2}CO\textsubscript{3}, formed by the decomposition of the electrolyte.\textsuperscript{8} From the results mentioned above, it is clear that downsizing POMs to the nanoscale and mixing with highly conductive carbon additives result in high capacity, which supports the low electronic conductivity of POMs. On the other hand, the capacity of nano-sized KPV fades gradually due to the surface catalytic activity of POMs.

In order to overcome these disadvantages, we coated the surface of nano-sized KPV with a conducting polymer. Polypyrrole (PP) was coated onto the surface of nano-sized KPV dispersed in ethanol. The thickness of the PP films is varied by changing the amount of raw materials for the polymer coating i.e., monomers and oxidant. The amount of SDBS and pyrrole, the monomers of PP, and iron chloride (III), the oxidant, used for coating is shown in Table I. The TEM image of PP-coated KPV is shown in Figure 4. It can be confirmed that the conducting polymer film covers the surface of KPV for all coating conditions. For samples A, B, and C, the thickness of the films is estimated to be 50, 30, and 10 nm, respectively. The film homogeneity of sample A and B is lower than that of sample C. Residual polymer that was not part of the surface coating was also observed in samples A and B. In contrast, a thin polymer film uniformly covers the surface of sample C in comparison with sample A and B. As shown in Figures 4, for samples A and B, the polypyrrole film has lower uniformity than the film on sample C, leaving more uncoated parts on the KPV surface. The uncoated surface of KPV nano-particles in samples A and B result in sub-reactions such as the decomposition of the electrolyte solution on the surface. This could cause the capacity to fade, as mentioned above. For sample C, the coated film with higher uniformity than sample A and B suppresses the sub-reactions at the surface and stable charge-discharge cycle performance is obtained.

In Figures 5c and 5d, the cycle stability of the n-KPV and PP-KPV systems at various current densities are plotted. At higher values of current density, PP-KPV shows high maximum capacity, as shown in Figures 5c and 5d: 410, 415, and 350 mAh g\textsuperscript{-1} at 167, 500, and 1000 mAh g\textsuperscript{-1}, respectively. This sample also showed good capacity retention, retaining 90%, 92%, and 93% of the maximum capacity for 370, 380, and 280 mAh g\textsuperscript{-1}, respectively. On the other hand, the maximum capacity of n-KPV decreased with the increase in the current density, e.g., 200 mAh g\textsuperscript{-1} at 1000 mAh g\textsuperscript{-1}. As seen in Figures 5e, the capacity of n-KPV at high values of current density is very low. The capacity fading of n-KPV proceeded more rapidly than PP-KPV at high current density. In particular, the capacity at 1000 mAh g\textsuperscript{-1} faded to below half of the maximum capacity after only 7 cycles. These results demonstrate that the conductive polymer coating on the surface of nano-sized POM effectively improves the rate performance and cycle stability at high current density. This suggests that the coated film on the POM surface suppresses the catalytic decomposition of the electrolyte solution and results in efficient transport of electrons in POM particles.

In Figures 6a and 6b, the Nyquist plots of n-KPV and PP-KPV are shown. In the OCV state before the discharge-charge, a single semi-circle was obtained for both n-KPV and PP-KPV with similar size; this can be ascribed to the charge transfer resistance. After the first cycle discharge-charge, the CTR values for n-KPV and PP-KPV are almost the same, while a new semi-circle appeared in the high-frequency region for PP-KPV. The two semi-circles for PP-KPV can be ascribed to the CTR for KPV and polypyrrole layer. After 10 cycles of discharge and charge, the resistance for n-KPV is much higher than that of PP-KPV. This steep increase in resistance for n-KPV may be caused by the rapid surface deterioration due to the surface reaction. On the other hand, the resistance for PP-KPV decreased in comparison with the initial state. This result indicates two things: 1) the polypyrrole coating suppresses surface deterioration and 2) the CTR decreases for KPV and the PP layer. This may be caused by the lithium-ion diffusion-path formation during the discharge-charge processes. The decrease of the CTR during the discharge-charge processes is reported.

| Sample | SDBS x g in 5 ml H\textsubscript{2}O | FeCl\textsubscript{3} y g in 5 ml H\textsubscript{2}O | Pyrrole z µl | thickness nm |
|--------|----------------|----------------|------|-----------|
| A      | 0.08           | 0.326                  | 260  | 10–50     |
| B      | 0.04           | 0.163                  | 130  | 5–30      |
| C      | 0.02           | 0.082                  | 65   | 5–10      |

Table I. Coating condition of poly- Pyrrole film on nano size KPV particle.

Figure 4. TEM images of PP-coated KPV under various conditions.
Figure 5. (a) Discharge-charge curves and (b) cycle stability of PP-KPV samples; (c)-(d) cycle stability of n-KPV and PP-KPV systems at various current densities.

Figure 6. (a) and (b) Nyquist plots of n-KPV and PP-KPV for charge-discharge process.
in our previous paper. The reason for this decrease in CTR with cycling is not clear now and it seems caused by the formation of lithium diffusion path in the crystal structure of KPV with the charge-discharge. In the following cycles, CTR continues to decrease. For PP-KPV, CTR decreases to about 70 Ω after 50th cycle, whereas that for n-KPV is still 1200 Ω. This difference in the AC-impedance spectra also supports the stable and rapid charge-discharge performance of PP-KPV.

Conclusions

In the present study, it was demonstrated that polypyrrole coating on the surface of nano-sized POMs can improve their capacity, cycle stability, and rate performance, overcoming major disadvantages such as low electronic conductivity and high surface reactivity. This method can be used for other active materials where the application of usual carbon coatings is difficult.

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References

1. M. S. Whittingham, Chem. Rev., 104, 4271 (2004).
2. B. L. Ellis, K. T. Lee, and L. F. Nazar, Chem. Mater., 22, 691 (2010).
3. A. Nykoi, A. Abouimrane, M. Armand, T. R. Gustafsson, and J. O. Thomas, Electrochem. Commun., 7, 156 (2005).
4. P. Barpanda, M. Ati, B. C. Melot, G. Rouesse, J.-N. Chotard, M.-L. Doublet, M. T. Sougrati, S. A. Cott, J.-C. Jumas, and J.-M. Tarascon, Nature Mater., 10, 772 (2011).
5. N. Sonoyama, Y. Suganuma, T. Kume, and Z. Quan, J. Power Sources, 196, 6822 (2011).
6. S. Uematsu, Z. Quan, Y. Suganuma, and N. Sonoyama, J. Power Sources, 217, 13 (2012).
7. E. Ni, S. Uematsu, Z. Quan, and N. Sonoyama, J. Nanoparticle Res. (2013).
8. E. Ni, S. Uematsu, and N. Sonoyama, J. Power Sources, 267, 673 (2014).
9. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, J. Electrochem. Soc., 143, 1114 (1996).
10. E. Ni, T. Kume, S. Uematsu, Z. Quan, and N. Sonoyama, Electrochem., 82, 14 (2014).
11. E. Ni, S. Uematsu, T. Tsukada, and N. Sonoyama, Solid State Ionics, 285, 83 (2016).
12. E. Ni, S. Uematsu, and N. Sonoyama, Solid State Ionics, 268, 222 (2014).
13. E. Ni, T. Tsukada, and N. Sonoyama, International J. Nanotechnology 31 (2016).
14. S.-Y. Chung, J. T. Bloking, and Y.-M. Chiang, Nature Mater., 1, 123 (2002).
15. H. Huang, S.-C. Yin, and L. F. Nazar, Electrochem. Solid-State Let., 4, A170 (2001).
16. P. S. Herle, B. Ellis, N. Coombs, and L. F. Nazar, Nature Mater., 3, 147 (2004).
17. P. P. Prosini, M. Lisi, D. Zane, and M. Pasquali, Solid State Ionics, 148, 41 (2002).
18. S. Kuroda, N. Tobori, M. Sakuraba, and Y. Sato, J. Power Sources, 119-121, 924 (2003).
19. Z. Bakeev and I. Taniguchi, J. Power Sources, 195, 7445 (2010).
20. L. E. Briand, G. M. Valle, and H. J. Thomas, J. Mater. Chem., 12, 299 (2002).
21. S. Himeno, M. Hashimoto, and T. Ueda, Inorg. Chim. Acta, 284, 237 (1999).
22. S. Himeno, T. Osakai, and A. Saito, Bull. Chem. Soc. Jpn., 62, 1335 (1989).
23. S. Himeno, T. Osakai, A. Saito, and T. Hori, Bull. Chem. Soc. Jpn., 65, 799 (1992).
24. M. T. Pope, Y. Jeannin, and M. Fournier, Springer-Verlag: Berlin Heidelberg New York (1983).
25. I. K. Kozhevnikov, Catalysis by Polyoxometalates 2, Wiley (2010).