Electronic conductivity is one of the critical factors that govern the performance of high-energy lithium-ion batteries. However, until now, equations have been used to simulate electrode behavior in the absence of the necessary experimental background. In this study, we examined whether or not two commonly used equations can be used to express the electronic conductivity of a positive electrode fabricated with an NCA-based material. The electronic conductivity of this positive electrode was comprehensively examined, and the experimental results were used to validate the two above-mentioned equations. It was revealed that (i) the electrode density and weight ratio of carbon black affect electronic conductivity in different ways and (ii) electronic conductivity is influenced by the volume fractions of both conductive carbon and active material. This deviation from classical percolation theory arises from the electronic conductivity of the active material, which cannot be regarded as an insulator. We therefore derived an empirical equation for a positive electrode composed of an NCA-based material. The empirical equation not only simulated the electrode more accurately, it also provides a better understanding of the electronic-conduction mechanism and helps to facilitate better electrode and battery design.

Electronic conductivity is one of the critical factors that govern the performance of high-energy lithium-ion batteries. However, until now, equations have been used to simulate electrode behavior in the absence of the necessary experimental background. In this study, we examined whether or not two commonly used equations can be used to express the electronic conductivity of a positive electrode fabricated with an NCA-based material. The electronic conductivity of this positive electrode was comprehensively examined, and the experimental results were used to validate the two above-mentioned equations. It was revealed that (i) the electrode density and weight ratio of carbon black affect electronic conductivity in different ways and (ii) electronic conductivity is influenced by the volume fractions of both conductive carbon and active material. This deviation from classical percolation theory arises from the electronic conductivity of the active material, which cannot be regarded as an insulator. We therefore derived an empirical equation for a positive electrode composed of an NCA-based material. The empirical equation not only simulated the electrode more accurately, it also provides a better understanding of the electronic-conduction mechanism and helps to facilitate better electrode and battery design.
Table I. Positive electrodes for electronic conductivity measurements.

| Weight ratio | AM\(^a\) | CB | PVdF | AM loading on one side [mg/cm\(^2\)] | AM density [g/cm\(^3\)] | Thickness on one side [μm] | Porosity | Volume fraction of CB, \(\varepsilon\) | Volume fraction of solid phase, \(\varepsilon_{sp}\) |
|--------------|---------|-----|------|-------------------------------------|-------------------------|----------------------------|----------|---------------------------------|-----------------------------|
| 85 1 (1.14 wt%) | 1.5 | 6.78 | 2.82 | 24.0 | 0.345 | 0.0185 | 0.625 |
| 85 2 (2.25 wt%) | 1.8 | 6.99 | 2.69 | 26.0 | 0.353 | 0.0352 | 0.613 |
| 85 5 (5.35 wt%) | 3.5 | 6.91 | 2.49 | 27.8 | 0.401 | 0.0326 | 0.568 |
| 85 10 (10 wt%) | 5 | 6.91 | 2.38 | 29.0 | 0.354 | 0.0777 | 0.589 |

\(\varepsilon\) AM, active material.

The electronic conductivity of a positive electrode is affected not only by the CB weight and the electrode density, but also by the CB structure.\(^8\),\(^25\) Therefore, in this mixing process, the viscosity of the slurry and the mixing time were kept as constant as possible to ensure the same degree of disintegration of the CB structure. The obtained electrode slurry was coated on both sides of an aluminum foil so that the loading of the active material on each side was \(\sim 7\) mg/cm\(^2\). The electrode sheet was dried at 180°C for 8 h and compressed to control the electrode density so that the porosity of the electrode was 0.3–0.5. Table I lists the final porosity and density of the active material for each electrode. After calendering, the electrode was vacuum-dried again at 180°C for 8 h. Electrodes with different weight ratios of conductive carbon and different active material densities were prepared for electronic conductivity measurements (Table I).

The four-point-probe method is typically used for measuring the electronic resistance of electrodes;\(^10\),\(^26\),\(^27\) however, this method has several issues. Because the electrode contact point is extremely thin, it is susceptible to the effects arising from local distribution of conductive additives. In addition, although the macroscopic direction of electron transfer during charge/discharge is the electrode thickness direction, the four-point-probe method can measure the electrode resistance in the direction parallel to the electrode sheet. Moreover, it is difficult to perform such measurements under pressure,\(^28\) and the interfacial resistance between the electrode and the aluminum current collector\(^29\),\(^30\) cannot be measured. To solve these issues, Wheeler’s group proposed a four-line-probe method,\(^31\),\(^32\) a superior approach that can measure in-line during the electrode fabrication process. However, it is difficult to employ this measurement method for laboratory use because it requires a special line probe and a simulation technique specific to the probe. In this study, the electronic resistance in the thickness direction of the electrode was measured using a simple two-electrode-based method as described by Thorat et al.\(^33\) Similar measurements have been recently reported.\(^28\),\(^33\)–\(^35\) One or two electrodes were sandwiched between two cylindrical indenters, and the direct current resistance was measured during the application of pressure. As this approach does not require any special probe or simulation, it avoids the above-mentioned issues associated with the four-point-probe method.

Two electrodes were cut out into 25-mm-diameter disks with rectangular protrusions and sandwiched between opposite indenters, as shown in Figure 1. The direct current resistance of the electrodes was measured using an electrochemical analyzer (ALS Model 660A, ALS Co., Ltd.). Before measuring the electronic resistance, the pressure inside the wound electrode ensemble of a house-made cylindrical cell was measured using a pressure measurement film (Prescale, Fujifilm), and it was found that a pressure of 2.45 MPa was applied to the electrode inside the wound electrode ensemble. Therefore, the applied pressure during the electronic resistance measurements was set as 2.45 MPa. Two measurements were performed for each electrode. The volume fraction of CB in the electrode was calculated from the weight ratio of the electrode components, the electrode density, and the electrode thickness using the true densities of the electrode components (4.651, 1.80, and 1.71 g/cm\(^3\) for the Mg-NCA active material, CB, and PVdF binder, respectively). Scanning electron microscopy (SEM; S-4300, Hitachi) was used to confirm the distribution and location of CB in the electrode.

Results and Discussion

To compare against the reported equations (Eqs. 1 and 2), the logarithm of the measured volume conductivity was plotted against two
different electrode parameters. Figure 2(a-1) shows a plot of the electronic conductivity logarithm of the electronic conductivity against the CB volume fraction in accordance with classical percolation theory (Eq. 1). On the other hand, Figure 2(b-1) shows the logarithm of the electronic conductivity against the volume fraction of the solid phase, which includes the active material and CB, in accordance with Eq. 2. Here, the sum of the volume fractions of the active material and CB is referred to as the volume fraction of the solid phase, which is determined as \((1 - \epsilon - \epsilon_b)\), where \(\epsilon\) is porosity and \(\epsilon_b\) is the volume fraction of the binder. Here, the sum of the volume fractions of the active material and CB is referred to as the volume fraction of the solid phase. The electronic conductivities of the electrodes having different electrode densities but the same weight ratio of CB were linear in both plots. The slopes of the straight lines differed with the weight ratio of CB, as indicated by different colors, and with electrode densities, as indicated by the same color, in Figures 2(a-1) and (b-1). The important inference drawn from these results is that the electronic conductivity depends quite differently on the electrode density and the CB weight ratio, although both influence the volume fractions of the CB and the solid phase.

Figure 2(a-1), which plots the electronic conductivity against the CB volume fraction, reveals that the electronic conductivities (1.50 and 1.68 S/m) of the two electrodes with 5.35 and 10 wt% CB differ by 12%, as indicated by the arrows, whereas the CB volume fraction differs by 51% (0.0707 and 0.1066). The percolation theory equation (Eq. 1), which has only one variable (i.e., the volume fraction of CB) is unable to explain such behavior. Furthermore, the two electrodes with 1.14 and 10 wt% CB, as indicated by the arrows in Figure 2(b-1), which plots electronic conductivity against the volume fraction of the solid phase, exhibit approximately the same solid phase volume fraction (0.545 and 0.553), while their electronic conductivities differ by more than three orders of magnitude (0.0086 and 11.1 S/m). This behavior is unable to be explained by Eq. 2, which is the most-used mathematical-simulation equation and only relies on the volume fraction of the solid phase as a variable.

The differences in the electrode-density and weight-ratio dependences of CB are discussed here on the basis of electrode structure. Figure 3 shows SEM images of the positive electrode with a CB content of 5.25 wt% and an active material density of 2.16 g/cm$^3$. The positive electrode is composed of large active material secondary particles (7 \(\mu\)m), fine CB particles (25 nm), and the PVdF binder. The large active material secondary particles constitute the basic framework of the porous electrode with the CB and binder located within...
the pores and junctions of the active material secondary particles (see Figure 3). Since the electrodes were fabricated by a wet process, the large-surface-area CB and the binder are integrated together owing to surface tension, and behave in a similar fashion to a CB/binder conductive polymer composite. The CB/binder composite accumulates in the channels of the rough surfaces of the active material secondary particles and at the junctions between the active material particles to form a conductive network in the porous electrode, as shown in the magnified image in Figure 3. Figure 4 shows a cross-sectional image of active material particles bound by the CB/binder conductive composite. The active material particles were closer together with increasing electrode density, and only the CB/binder conductive composite present at the junction was compressed. Hence, the volume fraction of the CB/binder conductive composite at the junction as well as its conductivity increased, although the conductivity at the active material surface was only marginally affected (Figure 3). On the other hand, the CB volume fraction in the entire CB/binder conductive composite changed with changing CB weight ratio, irrespective of location, and the connectiveness of the conductive network of the CB/binder composite changed. Hence, changes in the electrode density and the CB weight ratio affect the conductivity of the CB/binder composite at different places. Therefore, the relationship between conductivity and CB volume fraction changes with changing CB weight ratio and electrode density.

In summary, the positive electrode exhibited electronic conductivity that depended differently on electrode density and CB weight ratio. Therefore, we conclude that the two commonly used expressions (Eqs. 1 and 2) inaccurately express the electronic conductivity of a positive electrode composed of NCA-based active materials. Hence, we chose to derive an empirical equation that better expresses the correlation between the electronic conductivity and the electrode structure/composition of positive electrodes fabricated with NCA-based materials.

Here, empirical equations for the linear relationships between the logarithm of conductivity and the volume fractions of CB (Figure 2a-1) and the solid phase (Figure 2b-1) were derived. Interestingly, in both Figures 2(a-1) and (b-1), any linear relationship with the weight ratio of CB could have the same intercept on the y-axis.

Therefore, the following procedure was used to develop the empirical equations. First, an individual straight line was approximated for each weight ratio of CB using the least-squares method, and intercepts of these straight lines were obtained. Next, the straight line for each weight ratio of CB was approximated using the least-squares method with the intercept fixed as the average intercept (dotted lines in Figures 2a-1 and b-1). The approximated straight lines exhibited excellent agreement with the experimental values, as seen in Figures 2(a-1) and (b-1). The slope of each approximated straight line was plotted against the weight ratio of CB in Figures 2(a-2) and 2(b-2). The slopes in Figure 2(a-2) show linear relationships with the CB weight ratio, whereas the slopes in Figure 2(b-2) show logarithmic relationships with the CB weight ratio.

As shown in Figure 2(a-1), the volume conductivity of the electrode tended to approach the intercept value with decreasing CB weight ratio. Therefore, the intercept could be considered to be the volume conductivity of the electrode without the conductive additive. Hence, electrode conductivity, $\sigma [S/m]$, can be expressed by the following empirical equations:

$$\log \sigma = A_1 (w_c) \varepsilon_c + \log \sigma_0$$  \[3\]

$$\sigma = \sigma_0 \cdot 10^{A_1 (w_c) \varepsilon_c}$$  \[4\]

Here, $A_1 (w_c)$ is the slope, which is a function of the weight ratio of CB; $w_c$ [wt%] is the weight ratio of CB; $\varepsilon_c$ is the volume fraction of CB; and $\sigma_0$ [S/m] is the volume conductivity of the electrode without CB. The value of $\sigma_0$ is $7.613 \times 10^{-4}$ S/m when log $\sigma_0$ = $-3.1185$. To validate the intercept, we measured the electronic conductivity of the electrode without CB in a similar manner; however, because the electrode had an extremely large electronic resistance due to the large contact resistance between particles, large and significant variations were observed in the results. Therefore, it was impossible to determine the electrode conductivity without CB. A linear equation for the slope was obtained by the least-squares method as follows (Figure 2a-2):

$$A_1 (w_c) = -3.909w_c + 70.093$$  \[5\]

Substitution of $\sigma_0$ and Eq. 5 into Eq. 4 yields:

$$\sigma = 7.613 \cdot 10^{\varepsilon_c (-3.909w_c + 70.093) - 4}$$  \[6\]

Thus, the electronic conductivity was obtained as a function of the volume fraction of CB and the weight ratio of CB.

In the same manner, empirical equations for the relationship between conductivity and the volume fraction of the solid phase, as shown in Figure 2b-1, were obtained. The conductivity of the electrode is expressed by the following equations:

$$\log \sigma = A_2 (w_{sp}) \varepsilon_{sp} + \log \sigma_0$$  \[7\]

$$\sigma = \sigma_0 \cdot 10^{A_2 (w_{sp}) \varepsilon_{sp}}$$  \[8\]
Here, $A_2(w_c)$ is the slope, which is a function of the weight ratio of CB, and $\epsilon_{sp}$ is the volume fraction of the solid phase. The logarithmic equation for the slope (Equation 2(b-2)) was obtained by the least-squares method as follows:

$$A_2(w_c) = 2.6049 \ln w_c + 1.5838$$  \[9\]

Substitution of $\epsilon_{sp}$ and Eq. 9 into Eq. 8 yields:

$$\sigma = 7.613 \cdot 10^{(\text{2.6049} \ln w_c + 1.5838)-4}$$  \[10\]

Thus, the electronic conductivity was obtained as a function of the volume fraction of the solid phase and the weight ratio of CB.

The two obtained equations for the conductivity of the electrode as a function of the volume fraction of CB and the solid phase were validated by calculating the electronic conductivity for various weight ratios of CB and porosities (electrode densities) using Eqs. 6 and 10. First, to simplify these calculations, the relationship between the weight ratio of the binder and CB was determined. Over the entire range of CB weight ratios investigated (Table I), a linear relationship was obtained that connected both edges of the composition (CB:PVdF = 1:1.5 to CB:PVdF = 10:5). The weight ratio of the binder is related to that of the conductive carbon by:

$$w_s = 0.3889w_c + 1.1111,$$  \[11\]

where $w_s$ represents the weight ratio of the binder in the electrode. Figures 5a and 5b show the electronic conductivities calculated using Eqs. 6 and 10, respectively, for electrodes with 1–10 wt% CB and porosities ranging from 0.2 to 0.5. In Figure 5a, the conductivity initially increased with increasing CB weight ratio. However, above a CB weight ratio of 8 wt%, the conductivity decreased as the CB weight ratio increased. This behavior is impossible because the electronic conductivity of the electrode must increase with the amount of conductive carbon having the same porosity. In contrast, conductivity as a function of volume fraction of the solid phase increased continually with the weight ratio of CB (Figure 5b). From these results, we concluded that Eq. 10 was reasonable in that it expressed the conductivity as a function of volume fraction of the solid phase. In addition, this result indicates that the electronic conductivity of the positive electrode was influenced not only by the conductive carbon, but also by the active material. Thus, the conductivity could not be explained by classical percolation theory. Moreover, Eq. 10 requires a limitation on the range of the weight ratio of conductive carbon, $w_c$. When the weight ratio of the conductive carbon decreased to zero, Eq. 10 expresses the electronic conductivity of the electrode without the conductive carbon. Therefore, at this point, the slope should show a positive value because the electronic conductivity of the positive electrode without the conductive carbon should increase with increasing volume fraction of the active material. However, the natural logarithm of zero is undefined and the slope expressed by Eq. 9 became negative at $w_c \leq 0.544$ (Figure 2b-2). Therefore, the empirical equation obtained in this study (Eq. 10) does not accurately express the electronic conductivity for a small weight ratio of conductive carbon; i.e., less than 0.54 wt%.

The positive electrodes with Mg-NCA did not exhibit typical percolation behavior (Figure 2), whereas the electrode with LiMn$_2$O$_4$ reported by Mandal et al. exhibited percolation behavior.10 One reason for this difference in behavior involves the conductivity of the active material. As concluded above, electronic conductivity is influenced by the active material. The electronic conductivity of LiMn$_2$O$_4$ is $\sim 1.0 \times 10^{-3}$ S/m at room temperature.36 Unfortunately, the electronic conductivity of Mg-NCA has not been reported thus far; however, the electronic conductivity of LiNi$_{1/2}$Co$_{1/2}$O$_2$, whose composition is similar to that of Mg-NCA, was reported as $1.0 \times 10^{-4}$ S/m.35 Although the electronic conductivity of solid-solution materials might vary depending on the composition, the electronic conductivity of the Ni-based oxide is possibly greater than that of LiMn$_2$O$_4$. As LiMn$_2$O$_4$ has a much lower conductivity than that of conductive carbon, the active material can be regarded as an insulator. In contrast, Mg-NCA electrodes are considered to exhibit atypical behavior compared with that predicted by percolation theory because the semiconducting framework of Mg-NCA overlaps with the conductive network formed by CB. The obtained empirical equation (Eq. 10) was quantitatively applicable to the specific active material and CB investigated in this work because the intercept of the equation depends on the conductivity of the active material, and the slope depends on the shape, structure, and distribution of the CB. However, the basic system of this equation is applicable to other active materials and conductive carbon. Moreover, the empirical equation obtained for the positive electrode in this study not only provides more-accurate simulations, but also provides a better understanding of the electronic-conduction mechanism and helps to facilitate better electrode and battery design.

**Conclusions**

In this study, we investigated the electronic conductivities of positive electrodes with various CB contents and electrode densities in order to clarify the relationship between electronic conductivity and various electrode parameters. It was found that the electronic conductivity depended differently on the electrode density and the CB weight ratio. Therefore, it was concluded that the commonly used equations based on percolation theory and used for mathematical simulations do not adequately express the electronic conductivities of positive electrodes composed of NCA-based active material because these equations rely on only one volume-fraction variable for each component, namely the volume fractions of the CB and the solid phase.

Consequently, we successfully developed an empirical equation that describes the relationship between electronic conductivity and the volume fraction of the CB and the solid phase, which were found to reasonably express conductivity as a function of volume fraction of the solid phase. This result indicates that the active material influences the electronic conductivities of positive electrodes containing Mg-NCA; hence, the behavior of these electrodes does not obey the classical percolation theory. The empirical equation presented herein is expected to facilitate more accurate battery simulations and optimization of electrodes for high-energy batteries with low amounts of conductive carbon. Electrode and battery designs for high-energy applications will be optimized in our next study using this practical equation for the electronic conductivities of positive electrodes.

**ORCID**

Hiroki Kondo https://orcid.org/0000-0002-2708-9039

**References**

1. M. Park, X. Zhang, M. Chung, G. B. Less, and A. M. Sastry, *J. Power Sources*, 195, 7904 (2010).
2. A. I. Medalia and F. A. Heckman, *Carbon*, 7, 567 (1969).
3. J.-B. Donnet, *Carbon*, 32, 1305 (1994).
4. R. P. Kusy, *J. Appl. Phys.*, 48, 5301 (1977).
5. N. Johner, C. Grimaldi, T. Maeder, and P. Ryster, *Phys. Rev. E*, 79, 020104 (2009).
6. L. Pfland, A. Chang, S. Nazarenko, A. Hilnner, and E. Bier, *J. Appl. Polym. Sci.*, 76, 394 (2000).
7. J.-C. Huang, *Adv. Polym. Technol.*, 21, 299 (2002).
8. G. Liu, H. Zheng, X. Song, and V. S. Battaglia, *J. Electrochem. Soc.*, 159, A214 (2012).
9. D. S. McLachlan, M. Blaszewicz, and R. E. Newnham, *J. Am. Ceram. Soc.*, 73, 2187 (1990).
10. S. Mandal, J. M. Amorilla, J. Ibáñez, and J. M. Rojo, *J. Electrochem. Soc.*, 148, A24 (2001).
11. F. Gabbels, R. Jerome, P. Tressel, E. Vanlathem, R. Deltour, A. Calderone, V. Parente, and J. L. Bredas, *Macromolecules*, 27, 1972 (1994).
12. W. Zhang, A. A. Dehghani-Sanj, and R. S. Blackburn, *J. Mater. Sci.*, 42, 3408 (2007).
13. M. Doyle, T. F. Fuller, and J. Newman, *J. Electrochem. Soc.*, 140, 1526 (1993).
14. T. F. Fuller, M. Doyle, and J. Newman, *J. Electrochem. Soc.*, 141, 1 (1994).
15. J. Newman and W. Tiedemann, *ACES J.*, 21, 25 (1975).
16. M. Doyle and J. Newman, *Electrochem. Acta.*, 40, 2191 (1995).
17. P. M. Komulainen, J. W. Deidler, R. A. Dougall, and R. E. White, *J. Power Sources*, 116, 267 (2002).
18. K. Smith and C.-Y. Wang, *J. Power Sources*, 160, 662 (2006).
19. H. Kondo, Y. Takeuchi, T. Sasaki, S. Kawauchi, Y. Itou, O. Hiruta, C. Okuda, M. Yonemura, T. Kamiyama, and Y. Ukyo, *J. Power Sources*, 174, 1131 (2007).
20. K. Tatsuki, Y. Sasano, S. Muto, T. Yoshida, T. Sasaki, K. Horibuchi, Y. Takeuchi, and Y. Ukyo, *Phys. Rev. B*, 78, 045108 (2008).
21. T. Sasaki, V. Godbole, Y. Takeuchi, Y. Ukyo, and P. Novák, J. Electrochem. Soc., 158, A1214 (2011).
22. S. Muto, K. Tatsumi, Y. Kojima, H. Oka, H. Kondo, K. Horibuchi, and Y. Ukyo, J. Power Sources, 205, 449 (2012).
23. A. H. Tavakoli, H. Kondo, Y. Ukyo, and A. Navrotsky, J. Electrochem. Soc., 160, A302 (2013).
24. Y. Makimura, C. Okuda, T. Nonaka, Y. F. Nishimura, T. Sasaki, and Y. Takeuchi, ECS Electrochem. Lett., 3, A66 (2014).
25. S. Ahn, Y. Kim, K. J. Kim, H. H. Kim, H. Lee, and M. H. Kim, J. Power Sources, 81–82, 896 (1999).
26. C.-W. Wang, A. M. Sastry, K. A. Striebel, and K. Zaghib, J. Electrochem. Soc., 152, A1001 (2005).
27. Y.-H. Chen, C.-W. Wang, G. Liu, X.-Y. Song, V. S. Battaglia, and A. M. Sastry, J. Electrochem. Soc., 154, A978 (2007).
28. M. Indrikova, S. Grunwald, F. Gollks, A. Netz, B. Westphal, and A. Kwade, J. Electrochem. Soc., 162, A2021 (2015).
29. M. Gaberscek, J. Moskon, B. Erjavec, R. Dominko, and J. Jammnik, Electrochem. Solid-State Lett., 11, A170 (2008).
30. J. Illig, M. Ender, T. Chrobak, J. P. Schmidt, D. Klotz, and E. Ivers-Tiffée, J. Electrochem. Soc., 159, A952 (2012).
31. J. D. Flygare, A. A. Riet, B. Mazzeo, and D. R. Wheeler, J. Electrochem. Soc., 162, A2136 (2015).
32. B. J. Lanterman, A. A. Riet, N. S. Gates, J. D. Flygare, A. D. Cutler, J. E. Vogel, D. R. Wheeler, and B. A. Mazzeo, J. Electrochem. Soc., 162, A2145 (2015).
33. J. V. Thorat, T. Joshi, K. Zaghib, J. N. Harb, and D. R. Wheeler, J. Electrochem. Soc., 158, A1185 (2011).
34. W. Haselrieder, S. Ivanov, H. Y. Tran, S. Theil, L. Froboese, B. Westphal, M. Wohlfahrt-Mehrens, and A. Kwade, Prog. Solid State Chem., 42, 157 (2014).
35. W. Bauer, D. Nötzel, V. Wenzel, and H. Nirschl, J. Power Sources, 288, 359 (2015).
36. J. Molenda and W. Kucza, Solid State Ionics, 117, 41 (1999).
37. J. Cho, H. Jung, Y. Park, G. Kim, and H. S. Lim, J. Electrochem. Soc., 147, 15 (2000).