Influence of carbonaceous materials on electronic conduction in electrode-slurry

CrossMark

Mitsuhiro Takeno [a, b], Tomokazu Fukutsuka [a, c, *], Kohei Miyazaki [a, c], Takeshi Abe [a, c]

[a] Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[b] Automotive & Industrial Systems Company, Panasonic Corporation, Moriguchi, Osaka 570-8511, Japan
[c] Hall of Global Environmental Research, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

ARTICLE INFO

ABSTRACT

Carbonaceous materials have been used as conductive materials for the composite electrodes in lithium-ion batteries (LIBs). Since an increase in the amount of conductive material implies a decrease in the capacity of the LIB, the amount of conductive material used should be kept to a minimum. Carbonaceous materials as conductive materials have various morphology and crystallinity, therefore, the fundamental study of carbonaceous materials as conductive materials is important. In this study, the electronic conductivity of electrode-slurries and composite electrodes prepared using different carbonaceous materials (acetylene black (AB), fine graphite, and vapor grown carbon fiber (VGCF)) as the conductive material was investigated, and the effect of the different carbonaceous materials on the electron conduction network was discussed. In the electrode-slurry, AB and VGCF formed electron conduction paths and displayed high electronic conductivity. The electrode-slurry of AB displayed solid-like behavior, whereas the electrode-slurries of VGCF and graphite displayed fluid-like behavior. This difference influenced the electronic conductivity of the composite electrode.

1. Introduction

Lithium-ion batteries (LIBs) have been used since 1991 as the best type of rechargeable battery owing to their high energy density [1]. The demand for LIBs in mobile devices is due to their long duration of use and high energy density. Recently, much attention has been paid to LIBs as power sources for electric vehicles (EVs). In LIBs for EVs, their short charging time, in other words, their high rate performance, is an important issue, as well as their high energy density. Therefore, there has been extensive research into the high rate performance of LIBs [2—4]. To achieve high rate performance in LIBs, the reduction of the internal resistance in LIBs is essential. The internal resistance in LIBs is composed of electronic resistance and ionic resistance. Little research has been conducted concerning the electronic resistance in comparison to the ionic resistance. However, the electronic resistance is increasingly becoming recognized as the important factor for the rate performance of LIBs.

The composite electrode in LIBs is composed of an active electrode material, a conductive material, and a polymeric binder. Various active materials such as oxides, polyanionic compounds, graphite, and silicon have been used [5—12], and these materials, except for graphite, are classified as insulators or semiconductors. Therefore, the addition of a conductive material is essential to deliver electrons from the current collector to the active material in the composite positive electrode [13—15]. Although graphite exhibits higher electronic conductivity than other active electrode materials, a conductive material is added to decrease the inter-particle contact resistance of graphite. A simple way to provide sufficiently high electronic conductivity in the composite electrode is to use a large amount of conductive material. However, the volume of LIBs is limited, and an increase in the amount of conductive material implies a decrease in the amount of active electrode material, which leads to a decrease in the capacity of the LIB. Therefore, the amount of conductive material used should be kept to a minimum. Cheon et al. reported that the content of conductive material was related to the capacity and rate performance, and these two properties are inversely proportional to the content of conductive material [16]. Therefore, research into the electronic conductivity of the composite electrode is required.

The electron conduction paths in the composite electrode are

* Corresponding author. Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan..
E-mail address: fuku@elech.kuic.kyoto-u.ac.jp (T. Fukutsuka).

explained by the percolation theory [17]. In the percolation theory, the conductive material is regarded as a continuous phase. However, the interparticle contact resistance must be considered, because conductive materials exhibit several morphologies. In order to fabricate a composite electrode with superior rate performance, experimental analysis of the microstructure of the electron conduction paths should be performed. As conductive materials, carbonaceous materials such as carbon black (CB) are widely used, because CB is industrially mass-produced at low cost and displays relatively high electronic conductivity and chemical stability [13]. CB is composed of nanometer-sized carbon particles, which connect with each other and form clusters (aggregates and agglomerates). These connected structures act as an electron conduction network in the composite electrode. In addition, fine graphite powder is used as a conductive material owing to its high electronic conductivity [13]. Recently, vapor grown carbon fiber (VGCF) has been used in combination with CB [18].

Electron conduction networks prepared from various conductive materials are important. Although the effect of various conductive materials has been empirically examined in industrial and academic fields, fundamental research about the effect of carbonaceous materials as conductive materials on the electron conduction network in the composite electrode from the viewpoint of electronic conductivity has not been carried out. The electron conduction network in the electrode-slurry is also important because the composite electrode is prepared from an electrode-slurry composed of the active electrode material, the conductive material, a polymeric binder, and a solvent. In previous study, we proposed a new method of measuring the electronic conductivity of the electrode-slurry, and the relationship between the electronic conductivity of the electrode-slurry and the internal resistance was revealed [19]. In this study, the electronic conductivity of electrode-slurries and composite electrodes prepared using different carbonaceous materials (CB, graphite, and VGCF) as the conductive material is investigated, and the effect of the different carbonaceous materials on the electron conduction network is discussed.

2. Experimental

As conductive materials, acetylene black (AB, average primary particle size of 40 nm) from Denka Co. Ltd, graphite (KS-4, maximum particle size of 4 μm) from Timcal Ltd, and VGCF (average diameter of 150 nm and average length of 8 μm) from Showa Denko K.K. were used. The morphology of the conductive materials was observed by scanning electron microscopy (SEM, VE-9800, Keyence). The electronic volume resistivity of the conductive material was measured by the four-point probe method using a powder resistivity measurement system (MCP-PD51, Mitsubishi Chemical Analytech) at various densities.

Mg-doped LiCoO$_2$ (Mg-LCO) particles (average particle size of 6.5 μm and BET surface area of 0.43 m^2 g^{-1}) were synthesized from a mixture of Li$_2$CO$_3$ and Co$_3$O$_4$ doped with 2 mol% Mg by a solid-state method. The particle size and BET surface area of Mg-LCO were optimized for high-energy-density battery-use and these structural parameters were fixed in this study. The Mg-LCO particles were mixed with AB, polyvinylidene difluoride (PVdF) in 1-methyl-2-pyrrolidone (NMP), and NMP using a mechanical stirrer (T.K. HIVIS MIX model 2P-03). The weight ratios of the electrode slurry were Mg-LCO:conductive material:PVdF = 97:1:2, 96:2:2, and 95:3:2 wt%, respectively. The conductive material was kneaded with NMP at 95 rpm for 10 min and a "soft cake" was obtained. The "soft cake" was stirred with PVdF/NMP at 95 rpm for 10 min and was then stirred with Mg-LCO/NMP at 95 rpm for 10 min. The obtained electrode slurry was cast on a polyethylene terephthalate (PET) strip or aluminum foil. The electronic volume resistivity of the

composite layers on the PET strip was measured by the four-point probe method using a Loresta IP MCP-250 apparatus. In addition, the composite layer was peeled off from the PET strip, and the electronic volume resistivity of the composite layers was measured by an MCP-PD51 measurement system at a density of 3.3 g cm^{-3}.

The electronic volume resistivity of the electrode-slurry was measured by AC impedance spectroscopy utilizing a rheometer. The details were as mentioned in pervious paper [19]. In addition, measurements of steady-flow viscosity and dynamic viscoelastic behavior were carried out on the electrode-slurry at 25 °C with a strain-controlled rheometer to determine the viscosity as a function of the shear rate and the dynamic storage modulus (G') and loss modulus (G'') as a function of the angular frequency (ω). Cone plate fixtures with a gap angle of 0.02 rad and a plate diameter of 50 μm were used.

3. Results and discussion

Fig. 1 shows SEM images of the conductive materials. In Fig. 1a, aggregates and agglomerates composed of fine carbon particles are observed. In Fig. 1b, ca. 0.4 μm thickness graphite flakes with sizes of ca. 2–4 μm are aggregated. VGCFs are fibrous form and entangled as shown in Fig. 1c. These conductive materials displayed different morphologies, and the electron conduction network should be influenced by these morphologies. The electronic volume resistivities of the conductive materials (ρ_p) are plotted against the pellet density in Fig. 2. In all the conductive materials, ρ_p decreased with an increase in the pellet density, which was because the interparticle contact resistance decreased on pressing. The order of the ρ_p value is AB > graphite > VGCF at the same pellet density (ca. 1 g cm^{-3}) in Fig. 2. Because the electronic conductivities of graphite and VGCF are higher than that of AB owing to the difference in crystallinity [18], this order is reasonable. The reason why graphite had a higher ρ_p than VGCF is due to the orientation of graphite in the pellet. Oriented graphite pellets display anisotropic electron conduction; therefore, a higher ρ_p was observed. Next, the electronic volume resistivities of the electrode-slurries (ρ_{vs}) were measured and are plotted in Fig. 3. With an increase in the carbon content, ρ_{vs} decreased in all the conductive materials; however, the rate of decrease for graphite was low in comparison with VGCF and AB. The ρ_{vs} values of VGCF and AB were almost the same at all carbon contents and were less than the ρ_{vs} of graphite. The reason for this is thought to be that the electron conduction paths are formed by uniformly dispersed agglomerates and entangled fibers in AB and VGCF, respectively. In contrast, the particle size of graphite is considerably larger and the electron conduction paths are formed by interparticle point contact. Therefore, the amount of electron conduction paths did not increase with an increase in the carbon content. This result shows that the dispersion states of the conductive materials in the electrode slurries were remarkably different.

Aoki et al. reported the rheological analysis of a mixture of a carbonaceous material and a polymer, and the network structure was evaluated [20–23]. In the electrode slurry, the interaction between the conductive material and the polymeric binder was reported to be stronger than that between the conductive material and the active electrode material [24]. However, in this study, the content of the polymeric binder was fixed in all the electrode-slurries. Therefore, the rheological properties may reflect the difference in the conductive materials. Fig. 4 shows the data for the steady-flow viscosity of the electrode-slurry as a function of the shear rate. The variations in the values of G' and G'' of the electrode-slurry as a function of the angular frequency are shown in Fig. 5. The steady-flow viscosity is related to the structural viscosity, and G' and G'' are related to the dispersion structure of the slurry. The