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Application News

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Surface Observations

Lithium Ion Battery Binder Observations and Measurements of Physical Properties in Electrolyte Solution Using Scanning Probe Microscopy (SPM)

Introduction

Lithium (Li) ion batteries are used widely as rechargeable batteries in small electronic appliances such as digital cameras and mobile phones. Lithium ion batteries are also being developed for use in hybrid cars and electric vehicles, and further improvements are expected in terms of increased power output and battery performance. Lithium ion batteries are composed of a cathode, anode, separator and electrolyte, where the active material that comprises the cathode and anode are retained in place by the binder.

Normally the anode is made from a graphite active material, but recent years have seen research into silicon (Si) active materials as next-generation anode materials that will have a higher theoretical capacity than graphite active materials. Since Si anode active materials expand and contract substantially during charge and discharge as a result of incorporation and loss of Li ions, use of an Si active material for the anode makes the battery prone to breakage on repeated charge/discharge cycles and a short lifespan. To compensate for this issue, it is important to use a hard binder that is spread evenly in the battery to securely bind and retain the active material.

Here, we carried out SPM shape observations of binder samples held in both the electrolyte material used for actual battery operation and in N_2 gas for reference. The physical properties of binder samples were also measured in electrolyte to find the binder most suited to use in batteries with an Si active material as the anode.

Lithium Ion Batteries

Fig. 1 shows a diagrammatic representation of the principal behind lithium ion batteries operation. During charge, the charging current flows by the migration of Li ions from the cathode material, which is an Li compound, to the areas between layers of anode material. During discharge, the discharging current flows by the migration of Li ions from in-between the layers of the anode material into the cathode material.

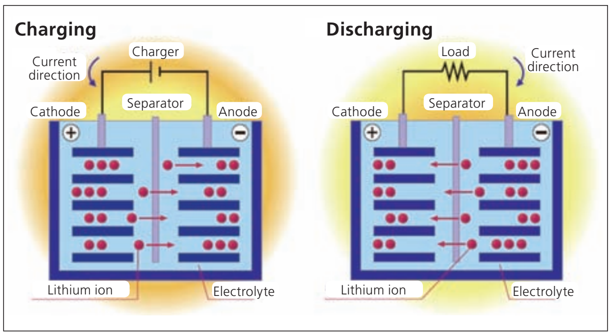

Fig. 1 Schematic of a Lithium Ion Battery

SPM-9700 Scanning Probe Microscope

The SPM-9700 scanning probe microscope is shown in Fig. 2. A scanning probe microscope is a microscope that observes the three-dimensional shape and local physical properties of a sample at high resolving power by using a microscopic probe (cantilever) that scans along the surface of the sample. A scanning probe microscope differs from an electron microscope in that it does not require a vacuum to perform its observations.

Fig. 2 SPM-9700 Scanning Probe Microscope

The SPM-9700 is capable of using a solution cell such as represented in Fig. 3 to perform SPM observations of a sample held in solution.

The SPM-9700 is also capable of SPM measurements in a gas atmosphere by using the environment controlled chamber shown in Fig. 4. This chamber is designed in the form of a glove box so samples can be prepared (cleaved, cleaned, dried, etc.) or exchanged within the controlled environment.

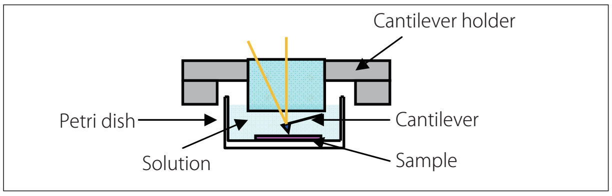

Fig. 3 Solution Cell Schematic

Fig. 4 Environment Controlled Chamber

Sample and Observation Conditions

The samples consisted of the three polyacrylic binders (1), (2) and (3) attached onto a glass substrate. Observations were carried out in an electrolyte (A) and in N_2 gas (B).

(A) Samples were immersed in a mixed solution of dimethyl carbonate (DMC) and ethylene carbonate (EC) that contained 1 mol/L of $LiPF_6$ for 24 hours. Observations were carried out after 24 hours while the sample remained immersed in the electrolyte.

(B) The above-mentioned samples were placed in the environment controlled chamber in a sealed state, and after replacing the atmosphere in the chamber with N_2, the seals on the samples were opened and observations performed in N_2 gas.

Observation Results

Three-dimensional images of samples (1), (2) and (3) as observed by SPM in electrolyte (A) and in N_2 gas (B) are shown in Fig. 5.

(A) A protuberance of about 10 nm was observed on sample (1) in electrolyte, while samples (2) and (3) were both flat. This result suggests samples (binders) (2) and (3) were distributed evenly in electrolyte.

(B) Samples (1) and (2) are flat when observed in N_2 gas, but a protuberance of 20 nm was observed on sample (3). This result differs from the results observed in electrolyte and demonstrates the importance of taking measurements in the actual use-case environment.

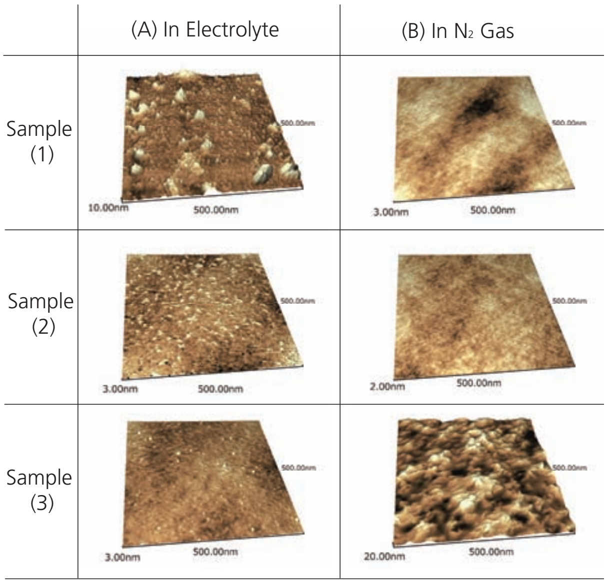

Fig. 5 Surface Morphology in Electrolyte and N_2 Gas (250,000 × magnification)

Force Curve Measurement

The concept of force curve measurement is illustrated in Fig. 6. The force acting on the probe (cantilever) is measured while varying the distance between the probe and the sample. A force curve is obtained by representing these measurements in graphical form. The relative hardness of samples as well as a quantitative measurement of sample hardness can be derived from the amount of probe deformation and probe slant when pushed against the sample.

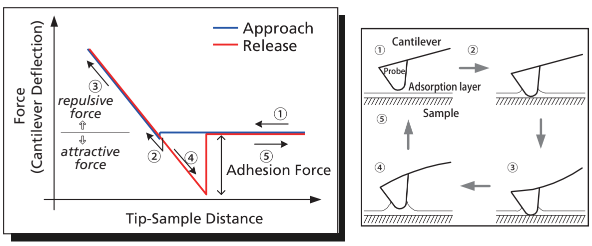

Fig. 6 Force Curve Measurement

Force Curve Measurement Results

Force curve measurements of samples (1), (2) and (3) in electrolyte are shown in Fig. 7. The region between ▼ and ▼ is the cantilever deflection measured when the probe is pressed about 15 nm towards the sample. The amount of binder deformation is obtained from the difference between the amount of indentation (Z Piezo Position) and amount of deflection of the probe.

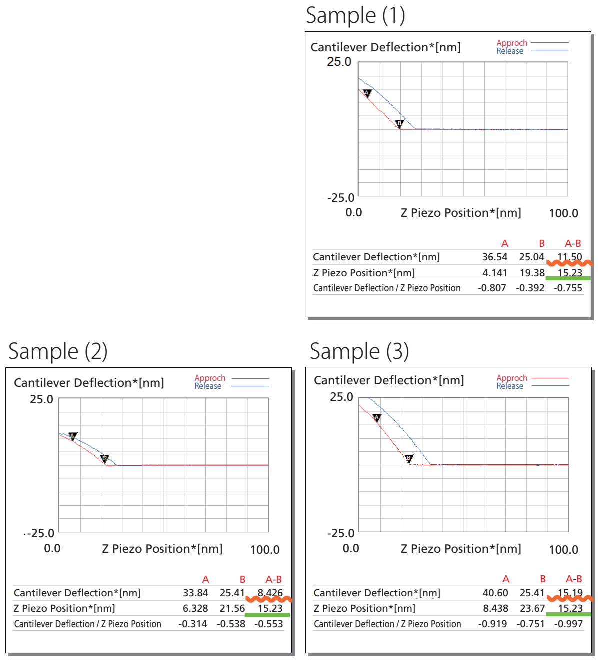

Fig. 7 Force Curve
Deformation = Z Piezo Position — Cantilever Deflection

Results for binder deformation are shown below. According to the results, sample (2) is the softest binder and sample (3) is the hardest.

	(1)	(2)	(3)
Deformation (nm)	3.7	6.8	0

From the observations of sample shape and force curve measurements, we found sample (3) to be the binder most appropriate for use with an Si anode active material. This is due to the evenness of the sample (3) binder and its relative hardness that will restrict expansion and contraction of an Si anode active material.

Conclusion

We succeeded in evaluating binders for lithium ion batteries in electrolyte, their use-case environment, from surface morphology observations and force curve measurements using the SPM-9700 scanning probe microscope. SPM is expected to increasingly contribute to research of battery materials.

Samples provided by the Komaba Group, Tokyo University of Science.

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