Lithium-ion batteries (LIBs) having a high energy density have been extensively used for consumer electronic devices such as cell-phones and laptop computers, moreover, the LIBs need even higher performance for the application to next generation electric vehicles and power stations. One of the biggest challenges for the large format LIBs is the safety, because the conventional LIBs use flammable electrolyte solutions. In order to minimize the safety concerns of the LIBs, solid-state lithium polymer batteries have been widely studied. In this study, the negative electrodes of graphite and silicon as active materials for solid-state lithium polymer batteries were investigated.

In part 1 is described the graphite negative electrode mixture of a spherical mesocarbon microbead (MCMB), a binder of polyethylene oxide (PEO) with Li(CF₃SO₂)₂N (LiTFSI) and a carbon conductive additive such as vapor grown carbon fiber (VGCF) and carbon nanotubes (CNTs). An electrode with MCMB, PEO⁻¹⁹LiTFSI and VGCF exhibits high reversible capacity of over 330 mAh g⁻¹, but poor cycling performance; the capacity retention was 71% at the 50th cycle. In contrast, the electrode with MCMB, PEO⁻¹⁹LiTFSI, VGCF and CNTs has an excellent cycling performance with a reversible capacity of ca. 310 mAh g⁻¹ and reversible capacity retention of 97% at the 50th cycle. The thin and long CNTs could be useful to maintain electrical contact in the electrode matrix during the volume change caused by lithium insertion and extraction into or from the MCMB. The effect of mixing process to the cycling performance of the spherical graphite negative electrode was also discussed. The optimum mixing speed of the electrode slurry was significantly dependent upon the choice of the conductive additives. In the case of the electrode with a VGCF as conductive additive, the electrode prepared at the low mixing speed of 5 m s⁻¹ showed an excellent cycleability compared with the one at the high mixing speed, while a CNT showed opposite trend, because of the dispersivity of the CNT. The well-dispersed CNT improved the contact among the MCMB, CNT and the PEO. An electrode containing both VGCF and CNT mixed at high speed showed further improvement in cycling performance. It suggested that the morphology of the conductive additive affects to the mixing condition of the slurry to obtain the optimum microstructure of the electrode which significantly affects to the cycling performance of the all-solid lithium ion batteries.
In part 2 is described the silicon negative electrode prepared with various binders and conductive additives. The electrode containing polyvinylidene fluoride (PVdF) and acetylene black (AB) showed a significant capacity decay in liquid electrolyte and polymer electrolyte. The electrode containing polyimide (PI) and carbon nanofibers (CNF) showed higher cycleability comparatively in liquid electrolyte, however, the reversible capacities decreased with cycling in polymer electrolyte. In order to investigate the mechanism of a rapid capacity fade in the polymer electrolyte, the cross sectional view of the half-cell in the polymer electrolyte was observed during a galvanostatic charge-discharge process by in situ SEM cell. The electrode containing PVdF and AB peeled off from the cupper foil. The electrode containing PI and CNF maintained a good adhesion with the cupper foil, however the electrode rolled back during the charge-discharge process resulting in the delamination of the lithium metal. On the other hand, the carbon paper electrode exhibited a good cycling performance of about 72% after 250th cycle, and the electrode did not show any change even after the cell operation for in situ observation. The 3D design of the electrode should be critical for solid-state lithium polymer battery to absorb the volume change of the silicon negative electrodes.