To address the increasing needs for electrical energy storage systems that can be implemented in electric vehicles and for renewable energy, a safe, low‐cost, high‐energy‐density and durable rechargeable battery system is in high demand. An all solid-state battery using solid electrolytes instead of organic liquid electrolytes is expected to have higher energy density than a lithium ion battery using organic liquid electrolytes and having a bipolar stack structure. Furthermore, use of solid state electrolytes will improve the safety and reliability of lithium secondary batteries. All-solid-state batteries can be divided into two types, thin-film-type and bulk-type. For large-scale applications, bulk-type lithium-ion batteries (ASSLBs) with high loadings of active material and solid electrolyte powders, are well-suited because of their high energy density. However, ASSLBs have crucial challenges for the practical applications, such as poor rate performance and poor contact between the active material and the electrolyte. In order to overcome the problem of low ionic conductivity in solid electrolytes such as LiPON, sulfide type electrolytes were developed. Sulfide-based solid electrolytes Li2S–P2S5 and Li2S–P2S5–GeS2 systems offer ion conductivity from 10-3 to 10-2 S cm-1 at room temperature, similar to liquid electrolytes; and they have a high decomposition potential of 5 V. With these electrolytes, the maximum resistance is observed at the cathode/sulfide electrolyte interfaces. Thus, understanding the cathode/electrolyte interface has become an issue of the greatest importance for the improvement in ASSLBs.