The performance of electrochemical devices (e.g., fuel cells and batteries) depends greatly upon the structure and microstructure of porous composite electrodes. It is well known that transport of ions and electrons, and in some cases multicomponent gas transport, can be very different from the intrinsic transport within the component phases. Because of great scale disparities between the complete electrode and its microstructure, effective transport properties (e.g., electronic and ionic conductivity) are required to model at the larger cell and system scales. A number of alternative approaches have been developed to model transport within porous electrode structures and to derive effective properties. Experimental techniques (e.g., focused ion beam—scanning electron microscopy, FIB