Graphene-based printed reference electrodes for next-generation lithium-ion batteries

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Reference electrodes are conceived to investigate the electrochemical characteristics of Li-ion battery (LIB) electrodes. The type, size, geometry, and position of a reference electrode in LIB play a key role causes measurement artifacts by geometric and electrochemical asymmetries, complicating a detailed impedance spectra analysis. In this work, novel flat and flexible printed reference electrodes based on lithium salts, namely lithium titanate and lithium iron phosphate, and single-/few-layer graphene (SLG/FLG) flakes are produced to reduce high-frequency measurement artifacts in mesh-like geometry and accurate monitoring of anode and cathode potentials separately in both static and dynamic (operando) conditions. The SLG/FLG flakes were preferred to other graphene-based materials (*e.g.* reduced graphene oxide) because of their excellent chemical purity (percentage atomic content of C > 95%), high electrical conductivity (e.g., carbon-paste with conductivity approaching 100 S cm^{-1}) and superior mechanical properties corresponding to an electrically conductive paste with low electrical resistivity (on the order of 0.01 Ω·cm).[1,2] The influence of the reference electrode coated on the separator together with an additional uncoated separator is analyzed using galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy (EIS). The electrochemical characterizations of two- and three-electrode pouch cells were compared to demonstrate that the insertion of a printed reference electrode does not affect the performance of the full cell. The printed reference electrode on the battery separator (Celgard 2500) is placed in the proper placement (between symmetrical electrodes) in the three-electrode pouch cell configuration. Pre-conditioning treatments are recommended also for these types of reference electrodes to obtain phases corresponding to their 50% of the state of charge, at which the change of potential with state of charge variation is approximately minimized. Plateau potentials in charge-discharge cycling curves were coincident with reported values (3.4-3.5 V for LFP and 1.5-1.6 V for LTO) in the literature.[3] The produced reference electrode shows long-term stability (more than 400 hours) because of graphene flakes' superior electrical and mechanical properties. The impedance contribution of the reference electrodes was properly modelled through a mesh-like electrical equivalent circuit. The obtained electrical modelling data confirm that all produced reference electrodes exhibit characteristic frequencies of more than 100 kHz, meeting the specifications requested for the EIS analysis of LIB half cells. The measured impedance of the whole cell exactly matched the sum of the measured impedances of the positive and the negative electrodes by the produced printed reference electrode.
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References

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