# EIS diagnostics of aged Li-ion batteries

M.J. Plancha*, P.P. Luz and C.M. Rangel

*Laboratório Nacional de Energia e Geologia, Paço do Lumiar 22, 1649-038 Lisboa, Portugal*

(*) e-mail corresponding author: mjoao.plancha@lneg.pt

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**Abstract**

High-power batteries with long cycling life and adequate storage behaviour are needed as energy sources devices for (hybrid) electric vehicles and lithium-ion rechargeable cells are the most promising candidates.

In this work, Li-ion cells with a nominal capacity of 10 Ah were studied. Electrochemical impedance spectroscopy (EIS) was used for studying the cycling ageing effect on discharge capacity fade. EIS measurements were conducted in a galvanostatic mode, by means of a Solartron Electrochemical Interface 1286 and a Solartron FRA 1250 controlled by Zplot from Scribner Associates. Scanning frequency ranged from 600 Hz to 0.005 Hz and the ac amplitude was set to 100 mA. An equivalent circuit complex non-linear least squares fitting procedure was used for spectra analyses.

Cell charge transfer and film resistances were estimated at several cycle life stages and its evolution on cycle number was analysed. Capacity losses were estimated after 300, 600 and 1200 cycles at C/1 discharge rate and were found to be 5.8, 7.5 and 16.8% of the initial capacity, respectively. EIS data revealed that the major factor responsible for the observed capacity fade was the cell's charge transfer resistance ($R_{ct}$) increase following the opposite tendency of the discharge capacity values with cycle number. Very little change can be attributed to film resistances as a result of ageing by cycling. The SEI layer thickness appeared to increase from 0 to 300 cycles remaining almost constant up to 1200 cycles.

The effect of a high storage temperature on the performance of the sealed commercial batteries was evaluated by means of discharge capacity measurements and impedance behaviour. The thermal ageing conditions were applied over time and the results were interpreted taking into account the cell's state of charge (SOC). Before storage at 45 $^oC$, in an open circuit state, cells were fully charged (100% SOC). At defined intervals, cells were cooled to ambient temperature and capacities were determined by a discharge step. As the cells aged up to 25 weeks at 45 $^oC$, the C/1 capacity slowly fades, at first, with a capacity retention of about 95% after 16 weeks of storage. However, the value of discharge capacity loss reached 10.9%, after 25 weeks (Fig. 1). Impedance data were fit to an equivalent circuit with a high frequency arc associated to the SEI film resistance ($R_{sei}$) and a second arc at medium frequencies to $R_{ct}$.

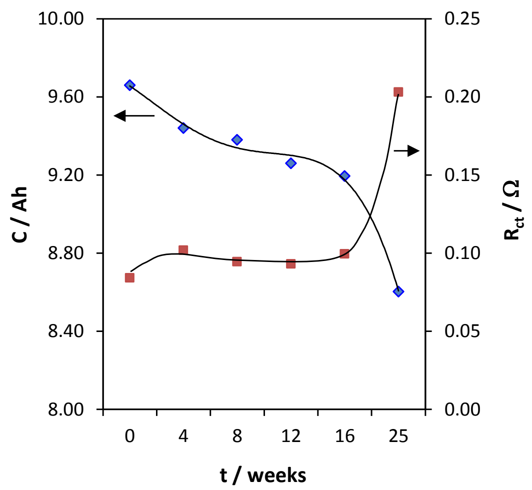


**Fig. 1.** C/1 discharge capacity and charge transfer resistance evolution with time of a Li-ion cell, at a storage temperature of 45 $^oC$.

A Warburg element associated with the solid-state diffusion of lithium ions was also present at low frequencies. The cell total impedance appeared to increase with the storage ageing time and the $R_{ct}$ parameter was observed to be the main contributor for this increase. The values of $R_{sei}$ obtained indicated a general growing of the SEI film up to 16 weeks at 45 $^oC$ storage, with the same $R_{sei}$ magnitude obtained for 25 weeks at 45 $^oC$. The relation between the capacity decay and the increase of the charge transfer resistance (Fig. 1) is discussed.

Generated heat in the various stages of cell life, during discharge/charge, was determined using an ARC calorimeter.