MECHANISM IDENTIFICATION IN LITHIUM-OXYGEN BATTERIES BY IMPEDANCE SPECTROSCOPY

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$Li\text{-}O_2$ batteries are claimed to be one of the future energy storage technologies because of their high energy density in comparison to any other type of batteries. Here Li^+ ions and O_2 directly react with each other. To produce a practical $Li\text{-}O_2$ battery with energy density around its theoretical value, the thermodynamic and kinetic mechanisms, which govern and limit their functioning, must be deeply understood.[1] In this study, $Li\text{-}O_2$ discharge process in different cathodes has been monitored by electrochemical impedance spectroscopy (EIS) [2, 3], in the presence and absence of O_2. When impedance spectra are recording from 4.0 to 2.7 V vs Li/Li^+, show the same behavior with and without O_2: it is observed an extended electrochemical double layer capacitance (EDLC) made up of adsorbed Li^+, which depends on the carbon matrix surface area. As soon as oxygen reduction reaction (ORR) voltages (~2.6 V) are tested in presence of O_2, the electrode shows a low-frequency capacitance increment accompanied of EDLC reduction. This functioning evidences that exists a competition between Li^+ surface adsorption and its consumption when ORR starts. Three steps with their characteristic reaction time and resistance in the $Li\text{-}O_2$ discharge could be identified: (i) interfacial phenomena, (ii) EDLC, and (iii) chemical capacitance generated by ORR. Noticeably EDLC remains unaltered after cycling. This fact suggests that the ORR products (Li_2O_2 and Li_2CO_3) are not covering the internal electrode surface, but deposited on electrode-O_2 interface, hindering thereby the subsequent reaction.
In conclusion, an equivalent circuit model is proposed to study the $Li\text{-}O_2$ batteries (figure 1.a), which affords to monitor adsorbed Li^+ consumption and reveal the evidence of Li^+ desorption from the C surface when the ORR starts.[4]

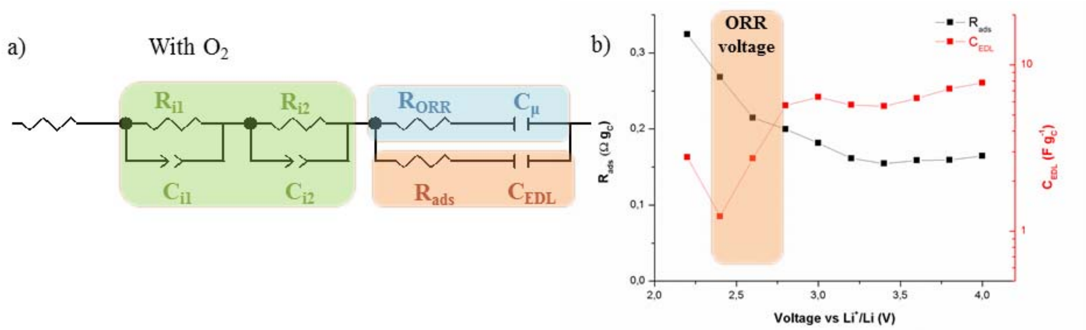

Figure 1. a) Equivalent circuit model for the system in presence of O_2: Green, interfacial phenomena; orange, EDLC; and blue, chemical capacitance ORR. b) Parameters determined during discharge process by the EIS fitting with the equivalent circuit model: resistance adsorbed Li^+, R_{ads}, and capacitance, C_{EDL}, associated to the formation of the EDL.

Reference to a journal publication:

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