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On measurement possibility of internal resistance of lithium sulfur cells by pulsed method

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An internal resistance of electrochemical cell is a significant parameter describing its properties. Often as a value of internal resistance is used its active resistance measured at a fixed frequency; usually it is 1 kHz [1]. This simple and universal method is could not be considered as correct because internal resistance of cell is not ohmic. Therefore the choice of measuring frequency of alternating current must be substantiated. It can be done under cell impedance spectrum. Quickly the impedance spectrum can be obtained by the pulsed method [2] when potential response on the current pulse is recorded. Then the impedance spectrum can be made from the step response *a(t)* by direct Fourier transform:

$$Z(j\omega) = a(0) + \int_0^\infty [(d/dt)(a(t))]\exp(-j\omega t)dt$$

As upper limit of integration we used value $T = 1/2f = \pi/\omega$ determined by the frequency at which impedance is calculated. It is equivalent to the computation of impedance at the first harmonic.

Experiments were made by the following way. Lithium sulfur cells were assembled by stacking sulfur cathode containing liquid electrolyte, separator (Celgard 3501) and lithium metal anode in stainless steel Swagelok® cells. Electrolyte was 1M solution of $LiCF_3SO_3$ in sulfolane. Electrochemical experiments were carried out at homemade potentiostat. The relative error of current stabilization was 0.1%. Potential was measured with accuracy of 10 μV.

The measurements were made by the following steps. When cell had achieved the preset discharge depth the current signal *I(t)* was added to the discharge current (fig. 1). The step response *U(t)* was recorded by discrete sampling with specified period. The spectrums were calculated in the frequency range 0.035 ÷ 5 Hz with resolution of 15 frequencies per decade.

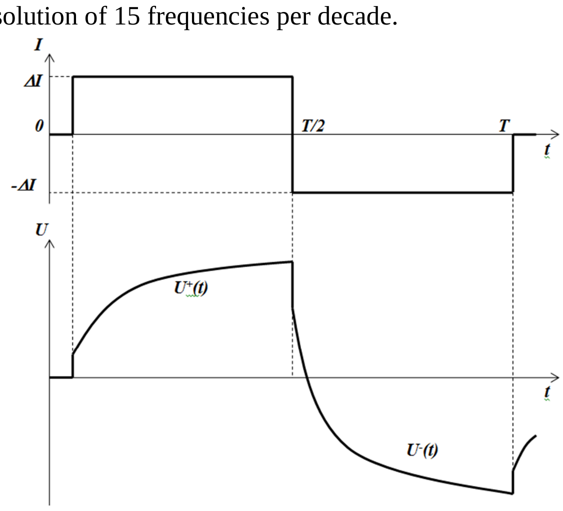

Fig.1. I(t) – applied signal, U(t) – response signal

The impedance hodographs of lithium sulfur cell are V-shape in the observable frequency range (fig. 2) independently on the discharge depth (fig. 3). Comparison of data obtained by pulsed method and the wideband impedance spectrums of lithium-sulfur cells [3-5] allows to conclude that recorded V-fragments of impedance are formed by crossing of semi-circle describing charge transfer resistance and low-frequency arm characterizing of diffusion within the cathode.

The dependence of resistance of lithium sulfur cell calculated by the minimum of impedance hodograph obtained by pulsed method on the discharge depth is the curve with maximum (fig. 3). The maximum resistance is observed at the maximum concentration of lithium polysulfide in electrolyte [5].

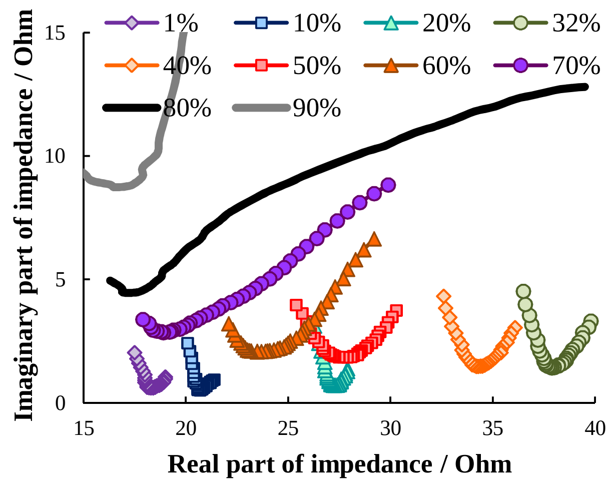

Fig. 2. Impedance of lithium sulfur cell. Frequency range 0.035 ÷ 5 Hz. Discharge depth is indicated in legend.

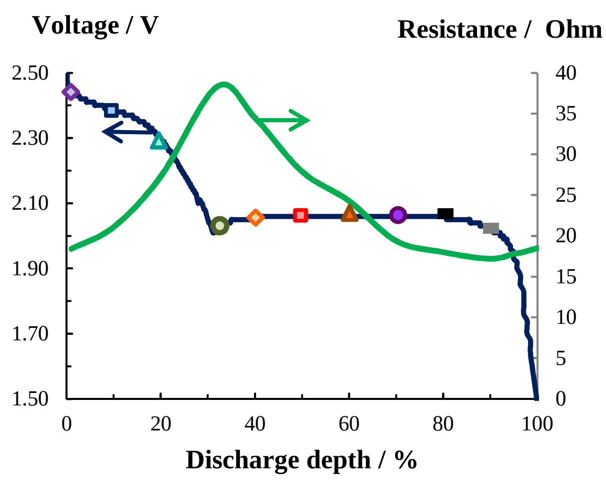

Fig. 3. Discharge curve of lithium sulfur cell. I = - 0.2 mA/cm^2, ΔU = 1.5 ÷ 2.8 V, t=30 ^{0}C

Thus it is shown that the internal resistance of lithium-sulfur cell can be measured by pulsed method. The impedance of lithium sulfur cell in frequency range 0.035 ÷ 5 Hz is practically ohmic and corresponds to the resistance of electrolyte and electrode reactions.

Literature

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