Comments on "State of Charge-Dependent Polynomial Equivalent Circuit Modeling for Electrochemical Impedance Spectroscopy of Lithium-Ion Batteries"

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A recent paper by Wang et al proposes a state of charge-dependent polynomial equivalent circuit model for lithium batteries. The model consists of an inductor, a Warburg element, a constant phase element (CPE) and two resistors [1]. Figure 1 shows the equivalent circuit model reproduced from [1].

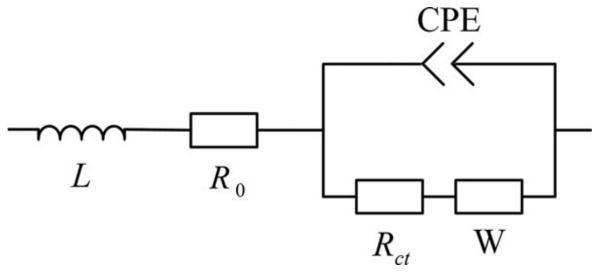

Fig. 1: Equivalent circuit model.

The authors quote the impedance equation of a Warburg element as:

$$Z_W = R_W \frac{tanh(j\omega\tau)^\phi}{(j\omega\tau)^\phi} \tag{1}$$

where τ is the diffusion time constant, ϕ varies between 0 and 1, and R_W is the Warburg resistance. This equation is wrong; in a Nyquist plot, the angle in a Warburg element is fixed to 45 degrees at high frequencies, corresponding to $\phi = 0.5$. Such behaviour is a result of diffusion through a semi-infinite medium [2]. The frequency band where it is observed is called the Warburg region. The correct impedance equation of a Warburg element is of the form [3], [4]:

$$Z_W = R_W \frac{tanh\sqrt{(j\omega\tau)}}{\sqrt{(j\omega\tau)}} \tag{2}$$

The authors cited [5] as a reference, but this paper contains no such equation.

In [1] the authors included both CPE and Warburg equations. The angle of the Warburg element, ϕ, was used as an independent variable to fit the measured data. Thus an extra, unjustified degree of freedom has been created. The authors managed to fit the model to their impedance spectra with an average mean absolute percentage error of 1.04%. We attribute the fitting success of the model to its having a total of 8 different parameters. Almost any model can be fitted to data with reasonable accuracy given sufficient degrees of freedom. Other researchers have obtained apparently 'good fit' where the accuracy is within 0.5% with quite different models, with a similar, excessive, number of parameters [6]. We refer readers to [7], [8] where it is shown that a single CPE and resistor model with a total of 4 degrees of freedom is capable of reproducing the impedance and charge-voltage characteristics of a lithium battery. The prediction was extraordinary with an accuracy of 0.5%.

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