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The Appearance of Unexpected Reactance Contributions in Systems Dominated by the Resistance – The Nature of Inductive and Capacitive Behaviour in Low Frequency Impedance Spectra of Corroding Electrodes, Batteries and Fuel Cells

C.A. Schiller[1], F. Richter[1], N. Wagner[2]

[1] ZAHNER elektrik, Thüringer Str. 12, D-96317 Kronach, Germany
[2] Institute of Technical Thermodynamics, German Aerospace Center (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany
cas@zahner.de

Some electrochemical systems may exhibit small inductive contributions to the overall frequency response, especially at low frequencies. Prominent examples are for instance corroding electrodes of Aluminium and Zirconium in the presence of chloride ions [1], mild steel in the presence of CO_2 at low pH value [2], high temperature fuel cells under certain load conditions [3], PEM fuel cells in the presence of carbon monoxide in the fuel [4] or rechargeable batteries under high current charging / discharging conditions. A lot of different mechanisms are discussed in the literature explaining very special situations, leading to inductive behaviour of electrochemical systems.
On the other hand, a very universal mechanism is able to explain the above examples and - beyond that - the appearance of low frequency capacitive loops in conjunction with the PEM membrane water balance.
Although some principal considerations can be found in literature [5], a comprehensive and thoroughly treatment is still outstanding so far.
In this paper a theory will be presented, which traces back the origin of unexpected low frequency reactance contributions in resistance dominated systems to the dependency of the Ohmic share of the impedance on a certain mediating magnitude.
For instance, this magnitude may be the effective electrochemically active area in the above mentioned example of the corroding electrodes and in the case of the CO-poisoned PEM anodes, the magnitude may be the temperature of the conducting material in the examples of the high temperature fuel cells and batteries and at least considering the example of the PEM, the magnitude may be the humidity of the membrane.
In all of these cases, the mediating magnitude influences the system's real part value of the conductivity, while the magnitude itself underlies long term changes caused by the electric magnitudes voltage or current. It is shown that the sign and the magnitude of the conductivity change and its relationship on voltage and / or current decides which kind of low frequency reactance is observed. A capacitive or an inductive controlled reactance may result and – moreover - even a negative real part of the impedance can be observed at the low frequency limit.
It has to be emphasized that the effects outlined above may be restricted to the resistive share and therefore, neither capacitances nor inductances must be involved necessarily.

The theory is proved and tested by means of different easily understandable objects which can reproduce quantitatively all of the above characterised regimes, depending on the relationship between mediating magnitude and conductivity.

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