Inductive Loops in Impedance Spectra of Polarized $SrTiO_3$ Thin Films: A Trace of Oxide Ion Motion Rather than an Experimental Artefact

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Several reasons may cause inductive loops in impedance spectra of solid state electrochemical systems. Some of them are simply artefacts due to instrumental effects [1] or due to an unfavorable sample set up [2]. In this contribution, we discuss inductive loops which represent true sample properties of oxide thin films. A detailed analysis of the loops even introduces a novel method for measuring the ionic conductivity of oxides with very low ionic transference number. Slightly Fe-doped $SrTiO_3$ (Fe:STO) thin films on a conducting Nb-doped $SrTiO_3$ substrate were investigated by means of impedance spectroscopy under DC voltages in the +/- 500 mV range. For all temperatures (ca. 300°C - 700°C) the applied bias voltage causes either an unusual "inductive loop" in the low frequency range of impedance spectra (see Fig. 1) or an additional semicircle. Moreover, current-voltage (I-V) curves strongly vary with changing scan rate and the shape of quickly measured I-V curves depends on the starting voltage.

All findings can be understood in terms of bias induced ion motion in the $SrTiO_3$ thin films: Upon a DC voltage, stoichiometry polarization takes place in the $SrTiO_3$ thin films which means that the oxygen vacancy concentration changes until an inhomogeneous steady state distribution is reached. For slowly measured current voltage (I-V) curves, each measurement point thus corresponds to a different oxygen vacancy profile in the film. I-V curves measured with fast scan rates, however, reflect the steady state established prior to the measurement. Accordingly, fast and slow I-V curves exhibit different slopes at one and the same voltage. This difference is again found in the impedance spectra since those probe the slopes of I-V curves. If slopes of fast curves are smaller than those of slowly measured curves, the low frequency resistance is smaller than that at medium frequencies and an "inductive loop" has to result. The frequency range of the loop indicates the time required for oxygen vacancies to redistribute after a voltage change.

Accordingly, the inductive loops (or additional arcs) measured upon bias are caused by ion motion in the films, even though the ionic current is very small compared to the electronic one. An equivalent circuit model is derived, which not only fits the spectra but can also explain the main features of all deduced parameters. Based on an estimate of the interfacial capacitance at the ion blocking electrode, such measurements can be used as a novel method for obtaining information on the ionic conductivity of mixed conducting thin films with very small ionic transference number. Similar effects are expected in many mixed conducting oxide thin films, provided time constants of stoichiometry polarization get into the frequency range of impedance measurements. Details are given in Ref. [3].

[1] G. Fafilek, Soid State Ionics 176 (2003) 223

[2] J. Fleig, J. Jamnik, J. Maier, and J. Ludvig, J. Electrochem. Soc. 143 (1996) 3636-3641

[3] S. Taibl, G. Fafilek, J. Fleig, Nanoscale 2016 (in press).

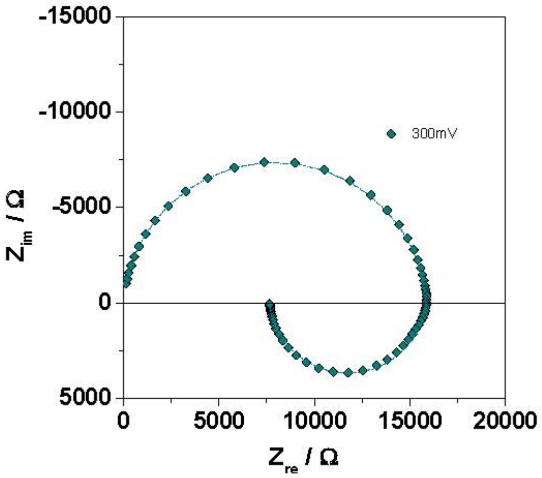

Fig.1: Impedance spectrum of a $SrTiO_3$ thin film measured at 620°C upon 300 mV bias voltage (top electrode $(La,Sr)CoO_{3-x}$, bottom electrode Nb-doped $SrTiO_3$.)