The Relation of Electrical Conductivity Profiles and Modulus Data Using the Example of STO:Fe Single Crystals: A Path to Improve the Model of Resistance Degradation

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Resistance degradation in perovskites is characterized by an increase in current over time with applied electric field. This behavior can be simulated and spatially resolved conductivity profiles can be measured, but some inconsistencies remain. A new approach to address these problems is presented that utilizes time-resolved impedance spectroscopy with an applied DC voltage to provide new insight into the resistance degradation phenomenon. In particular, this method allows the *in-situ* acquisition of spatio-temporal variations in conductivity. In SrTiO₃ a single bulk-dominated maximum of the imaginary part of the modulus M'' transitions to two maxima during degradation, reflecting the hole conductivity in the anode region and the electron conductivity in the cathode region. To clarify the influence of conductivity profiles on impedance data, the reversed route is presented by using simulated conductivity profiles to calculate impedance data. It will be emphasized that this methodology is not limited to the perovskite system considered here, but can be adapted to any kind of system characterized by a spatially varying conductivity.

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1. Introduction

Within the last several decades a detailed description of the resistance degradation process in perovskite-type systems such as SrTiO_3 and BaTiO_3 has been presented [1–16]. In particular, the defect chemistry of iron-doped SrTiO_3 (STO:Fe) was investigated [7–10] since it is a model system to study resistance degradation and redox-based resistive switching devices [14,17]. Baiatu *et al.* [2] formulated the first comprehensive numerical model for STO:Fe revealing that oxygen diffusion is the major source for resistance degradation. During resistance degradation oxygen vacancies accumulate at the cathode side resulting in an n-type cathode and a p-type anode region as well as a color change where both regions meet. The anode region turns dark since most of the iron atoms change their oxidation state from Fe^{3+} to Fe^{4+} [18]. Numerical simulations were able to reproduce the decrease in resistance [19] by around two orders of magnitude, which can be alternatively illustrated as an increase in current density [2] or effective conductivity [20]. However, current density only reflects the rate limiting impact of slices positioned in series and thus the more resistive regions in the single crystal. This argument will be confirmed within this paper by simulating the total conductivity with different values of the electron mobility. It will be shown that the more resistive region is the anode region. Consequently, one can only assume that the model introduced by Baiatu [2] reflects the alteration of the hole conductivity well, but it is not ensured that the correct electron conductivity is considered in the cathode region. The fact that the simulated conductivity in the cathode region yields unexpectedly high values and this region should behave like a metal [4,21] is particularly addressed by Rodewald [3] and Liu [4]. However, both approaches differ significantly, since the electron conductivity σ_n is given

according to Equation 1 as the product of electron concentration c_n , electron mobility μ_n , and the elementary charge q . Hence, the cause for a change in conductivity could be related to either a change in μ_n , c_n , or both.

$$\sigma_n = qc_n \mu_n \quad (1)$$

Two main scenarios which could take place in the cathode region during degradation are controversially discussed. Rodewald *et al.* [3] measured the conductivity profile after degradation with a variety of microcontacts. To match the measured and simulated conductivity profiles, they assumed that the reduction in conductivity is due to a decrease in electron concentration caused by the reaction of electrons with doubly charged oxygen vacancies to singly charged oxygen vacancies. Although this adjustment of the model was explicitly excluded by Baiatu *et al.* [2] the occurrence of singly charged oxygen vacancies was found to be reasonable in reduced STO in the considered temperature range [7,8]. On the contrary, Liu *et al.* [4] argued with the formation of small polarons [22–24] in the cathode region since a parallel conduction branch was found by immittance spectroscopy, with an activation energy of 0.1 eV. Thus according to Liu *et al.* [4] the electron mobility might be reduced. Furthermore, Liu *et al.* [4] pointed out that transforming the impedance data to modulus data is the best way to study degraded STO:Fe single crystals since they exhibit regions with different conductivity connected in series [4,25]. The weakness of both studies is that the measurements were taken after the degradation voltage was turned off, which allows for partial re-equilibration relaxation of the oxygen vacancies. This is evident since both studies measured a bulk region which is not existent in the final degraded state [2,20]. In

the presented paper, the process of re-equilibration is termed recovery and will be discussed in more detail using time-resolved modulus data.

STO:Fe single crystals were chosen to exclude any influence of grain boundaries and domain walls on the electrical properties. Thus the interpretation of measured and simulated data allows the simplification of a predominant one-dimensional current flow and a homogeneous initial, undegraded state. Spatial inhomogeneities are predominantly introduced during degradation by oxygen vacancy diffusion caused by an applied electric field [19,20].

First, this article will present the measured immittance data during degradation and recovery. Then correlations between simulated conductivity profiles and modulus data will be demonstrated. This includes the clarification of the frequency-dependent features that are related to either the bulk, anode, or cathode region. Using these insights a better comprehension of the degradation process is elaborated in regard to assumptions made by Baiatu [2,19], Rodewald [3], and Liu [4]. The conclusions drawn here will be supported by comparing the influence of different magnitudes of electron conductivity in the cathode region on the effective conductivity vs. time behavior as well as on the modulus data in the degraded state. Finally, a prediction of the conductivity profile based on measured modulus data will be given.

2. Experimental Procedure

High-purity iron doped SrTiO₃ single crystals (0.01 wt. % Fe) were purchased from MTI Corporation. The STO single crystals exhibited an electrode area and thickness of 3×3 mm² and 0.5 mm, respectively. Both electrode planes were optically polished before annealing for 12 h at an oxygen partial pressure of 2×10⁻⁵ bar and 900 °C and subsequent quenching to

room temperature. The electrodes were deposited using DC sputtering of platinum. The in-situ degradation and recovery studies were performed at 210 °C using an Agilent 4284A LCR Meter with an AC amplitude of 1 V and a DC voltage of up to 40 V.

3. Results and Discussion

3.1. *In-situ* immittance measurements

The DC voltage profile which is used to obtain immittance data during degradation and recovery is given in Figure 1. Here, immittance is used as a general expression for impedance, admittance, complex dielectric constant, and complex electrical modulus [26]. At first the initial, undegraded state is measured using $V_{DC}=0$ V. Then a DC voltage of 40 V is applied and continuous impedance measurements are performed until the degradation process is finished. Finally, the DC voltage is turned off to record the change in impedance during the recovery process. The temperature is kept at 210 °C at all times.

The measured complex impedance Z^* is converted to the modulus M^* according to Equation 2 [27].

$$M^* = j2\pi f C_0 Z^* \quad (2)$$

Here, the parameters are frequency f , $j = \sqrt{-1}$, and the capacitance of free space $C_0 = \epsilon_0 A / d$ containing the electrode area A , the distance between the electrodes d , and the permittivity of free space ϵ_0 .

The utilized technique of in-situ immittance measurements is comparable to degradation studies on STO:Ni single crystals performed by Waser [5]. However, the following analysis will highlight the benefits for analysis due to transformation of impedance to modulus data as well as the gain of knowledge about changes of conductivity within the entire single crystal

due to a comparison of modeled and measured data. The impedance data was tested for plausibility utilizing the Kramers-Kronig test [28,29] (see supplementary information). While most of the data ($t = 0$ s and $t > 1500$ s) exhibits high quality data with negligible deviations (< 0.3 %), there is a slight deviation (< 4 %) observed at the beginning of the degradation since the system is changing due to oxygen vacancy diffusion on a similar time scale as the acquisition time of one frequency sweep. As the real time degradation process is discussed qualitatively below, these slight deviations do not affect the given conclusions.

3.1.1. The degradation process

In Figure 2 impedance and modulus are plotted in complex planes showing data recorded during degradation. For the initial, undegraded state both impedance and modulus exhibit a perfect semi-circle indicating one distinct relaxation frequency [27]. This corresponds to a homogeneous conductivity dominated by oxygen vacancy diffusion [9,30,31] and will be validated below. With proceeding degradation the semi-circle plotted as impedance becomes smaller indicating a decrease in resistance. It also becomes depressed indicating a distribution of relaxation times [27]. When plotting the same data using the modulus formulism it is furthermore evident that this distribution of relaxation times must have two predominant relaxation frequencies leading to two semi-circles. Since the modulus and in particular the imaginary part M'' as a function of frequency highlight the features of degraded STO:Fe most suitably [4,25], the following studies will focus on this type of representation. In addition, the impedance data in Figure 2a) show that only the high-frequency semi-circle is observed in the measured frequency range. Thus under the conditions studied the AC signal only covers ionic

and electronic relaxation, but no migration of Warburg type [30–32]. The long-range migration of oxygen vacancies consequently only results from the applied DC voltage.

Figure 3 correlates the commonly shown current density as a function of time with frequency dependent modulus data $M''(f)$ at different stages of degradation. As demonstrated by West *et al.*[33] the analysis of frequency dependent immittance data needs to be carried out on logarithmic scales since the slope of the spectra ($S = \partial \log M''(f) / \partial \log f$) contains valuable information about the distribution of relaxation times, which will be elaborated in the following. Neglecting Warburg diffusion, the mixed conductor STO can be described as a parallel capacitor and resistor at which the resistor is defined as total resistance given by the ionic and electronic resistance positioned in parallel [30]. In case of a parallel resistor and capacitor element the relaxation frequency f_r can be correlated with the conductivity σ using Equation 5 as well as Equation 3 and 4.

$$R = \frac{d}{\sigma A} \quad (3)$$

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \quad (4)$$

$$f_r = \frac{1}{2\pi RC} = \frac{\sigma}{2\pi \varepsilon_0 \varepsilon_r} \quad (5)$$

Here, R is the resistivity and ε_r the relative permittivity, which is measured to be $\varepsilon_r = 192$ at 210 °C for the studied sample. The experiments were carried out at 210 °C ensuring that all relaxation peaks are within the measured frequency range of 40 Hz to 1 MHz (see Figure 3).

The impedance Z^* of a single equivalent circuit element consisting of a resistor and a capacitor in parallel is given in Equation 6. Here the imaginary component X_i is related to the capacitance via Equation 7.

$$Z^* = Z' + jZ'' = \frac{R_i X_i^2}{R_i^2 + X_i^2} + j \frac{R_i^2 X_i}{R_i^2 + X_i^2} \quad (6)$$

$$X_i = \frac{1}{2\pi f C_i} \quad (7)$$

Consequently, the real part of the modulus $M'(f)$ and imaginary part of the modulus $M''(f)$ of an RC element can be described by inserting Equation 3, 4, and 7 in Equation 6 and transformation to the modulus formulism by Equation 2.

$$M' = \frac{(2\pi f \varepsilon_0)^2 \varepsilon_r \Delta x}{((2\pi f \varepsilon_0 \varepsilon_r)^2 + \sigma^2) d} \quad (8)$$

$$M'' = \frac{2\pi f \varepsilon_0 \sigma \Delta x}{((2\pi f \varepsilon_0 \varepsilon_r)^2 + \sigma^2) d} \quad (9)$$

In Equation 8 and 9 Δx is used to consider the subdivision of the STO single crystal into n slices with equal width, but different conductivity, which will become important later. In the case of homogeneous conductivity as given for the initial undegraded state Δx can be assumed to be equal to d . Considering the threshold of low and high frequencies in Equation 9 it is possible to determine the slope S below ($S=+1$) and above ($S=-1$) the relaxation frequency f_r .

The $M''(f)$ spectrum of the initial, undegraded state of STO:Fe in Figure 3b) is characterized by one distinct maximum and nearly perfect slopes of $S=+1$ and $S=-1$ on both sides of the maximum. Thus there is only one distinct relaxation frequency f_r at 200 Hz resulting in $\sigma = 2.1 \times 10^{-8} \text{ S cm}^{-1}$ using Equation 5. This value agrees with that calculated ($\sigma = 1.8 \times 10^{-8} \text{ S cm}^{-1}$) using mobility and charge carrier densities (given by the defect chemistry [20]) for the conditions described in section 2 and used for subsequent simulations.

The most important implication of Equation 5 is that the relaxation frequency f_r is proportional to the conductivity within the considered RC element. Consequently, a shift of the maximum of the $M''(f)$ spectrum to higher frequencies or an increase in f_r can be correlated to an increase in conductivity. The variation of f_r due to a change in permittivity is neglected since the applied voltage is too low to cause significant soft mode hardening effects [34] and the change in conductivity will be at least two orders of magnitude higher.

At the beginning of the degradation process the $M''(f)$ spectrum in Figure 3b) shifts to higher frequencies by one order of magnitude and is characterized by a small shoulder at higher frequencies. Since no maximum is observed at 200 Hz anymore the conductivity within the complete single crystal must have been increased by at least one order of magnitude ($\sigma \approx 2 \times 10^{-7} \text{ S cm}^{-1}$). The shoulder indicates that there are regions with even higher conductivity. These regions are most likely the electrode interface regions. This result agrees very well with measurements of local conductivity during degradation performed by Raith *et al.* [6]. With proceeding degradation the distinct maximum $M''(f)$ which was observed at first, is continuously transformed into two maxima. Here, the maximum at lower frequencies ($f_r \approx 9 \text{ kHz}$) corresponds to the anode region, while the maximum at higher frequencies ($f_r \approx 400 \text{ kHz}$) is related to the cathode region. Thus the conductivity during resistance degradation increases by less than two orders of magnitude in the anode region, whereas it increases by more than three orders of magnitude in the cathode region. The bulk region completely vanishes as it is turned into the anode and cathode region. The relevance of the different magnitudes of the two maxima as well as the assignment to anode and cathode region will be explained below, when the simulation of the $M''(f)$ spectra is introduced.

3.1.2. The recovery process

The changes in the spectra of $M''(f)$ during the recovery process are shown in Figure 3c). The recovery process is dominated by the back-diffusion of oxygen vacancies from the cathode to the anode side driven by the concentration gradient. Thus the entire change in $M''(f)$ results without an applied electric field within an observed time range of 6 h at 210 °C. After 6 h the maxima caused by the anode and cathode region have disappeared completely and the $M''(f)$ spectrum is nearly identical to the initial, undegraded state characterized by one bulk feature with homogeneous conductivity at 200 Hz. Consequently, given sufficient time, a degraded STO:Fe single crystal can recover at 210 °C. A similar observation showing the reversibility of the increased conductivity due to degradation is reported for Mg-doped SrTiO₃ ceramics [35]. The recovery process is expected since Liu *et al.* [36,37] demonstrated that reasonable oxygen migration occurs for temperatures $T > 80$ °C using thermally stimulated depolarization currents (TSDC). This result is very important for the evaluation of the findings of Rodewald [3] and Liu [4], since in both cases the investigations were carried out after the degradation voltage was turned off. The modulus data of Liu *et al.* [4] is comparable to the ones shown in Figure 3c) recorded just before the fully recovered state. Therefore it can be concluded that the STO:Fe single crystal characterized by Liu *et al.* [4] is mainly recovered and the anode and cathode regions are assumed to be too small. Rodewald *et al.* [3] observed a much smaller bulk region than Liu *et al.* [4], which might be comparable to the first or second measurement after the voltage is turned off in Figure 3c). Beyond dispute, Rodewald [3] contributed valuable information by being the first to display experimentally the conductivity

profile within an STO:Fe single crystal. However, measurements performed by Rodewald [3] do not represent the fully degraded state either.

In addition, the measured spectra shown in Figure 3 during degradation and recovery allow a detailed and very valuable insight into the dynamics of these processes. The main benefit results from the fact that during recovery no external field is applied that could affect the redistribution of oxygen vacancies, electrons, and holes. Consequently, the degradation process must be seen as a superposition of drift and diffusion, whereas the recovery process is only driven by diffusion and possible internal fields. Thus it is most likely that changes in the dynamics can be correlated to the impact of drift effects. One example might be the increase of conductivity in the complete crystal at the beginning of the degradation without the formation of distinct anode and cathode regions. However, during recovery the bulk region immediately exhibits the low conductivity as observed for the initial state. Consequently, the applied electric field must impact the conductivity in the bulk region during degradation. On the contrary, the conductivities in the anode and cathode region do not change significantly upon turning off the voltage suggesting these might not be influenced by the electric field. The slightly reduced electron and hole conductivities (the maximum shifts to lower frequencies) during the recovery process might be connected to a decrease in charge carrier density with a gradual decrease of cathode and anode width, respectively.

3.2. Simulation of immittance data during degradation

The simulations shown in the following are performed using the formalism introduced by Baiatu *et al.* [2] and reviewed by Wang *et al.* [20] Based on literature values for electron, hole, and oxygen vacancy mobilities [9,38] as well as their calculated concentration profile

[2,20], these simulations allow the determination of spatially resolved total conductivity profiles for each time interval during degradation. Relevant parameters are given as supplementary information. Using these simulations Baiatu [2] calculated the time dependent increase in current density during degradation and matched this with measurements. However, this approach is not sufficient to prove the validity of the proposed model since many conductivity profiles lead to the same current density vs. time behavior. This will be shown in Figure 5. Before discussing the results in detail, the procedure of calculating modulus spectra using simulated and spatially resolved conductivity data will be presented to understand the characteristics of $M''(f)$ data shown in Figure 4. However, based on the results in Figure 5 the electron mobility was chosen four orders of magnitude lower than the free electron mobility given by Denk *et al.* [9] to reconcile the conductivity that was observed experimentally here and also by Rodewald [3]. As described by Equation 1 changing the charge carrier density or changing the electron mobility will have the same effect on the electronic conductivity. To verify one or the other, more precise simulations of the time dependence during degradation and at different temperatures need to be performed. This publication is the first to cover the complete ionic and electronic properties of the entire single crystal experimentally. Thus this publication concentrates on the correct interpretation of the degradation data, and it is not the intent to provide a conclusive revised theory about the origin of conductivity reduction in the cathode region.

To calculate the frequency dependent immittance data from simulations, the same partition model as used by Baiatu [2] to calculate the oxygen vacancy flux can be utilized. In this case the STO:Fe single crystal is sliced into n slices with equal width Δx . Each slice can then

be expressed by a parallel connection of a specific conductivity that can be transformed into a resistance value R_i (Equation 3) and a relative permittivity that can be transformed into a capacitance value C_i (Equation 4). Since the impedance of series-connected elements can be superposed, the real part of the impedance (Equation 10) as well as the imaginary part of the impedance (Equation 11) for the entire single crystal can be determined by summing up all slices within the STO:Fe single crystal.

$$Z' = \sum_{i=1}^n \frac{R_i X_i^2}{R_i^2 + X_i^2} \quad (10)$$

$$Z'' = \sum_{i=1}^n \frac{R_i^2 X_i}{R_i^2 + X_i^2} \quad (11)$$

The resulting imaginary part of the modulus (Figure 4c)) or any other immittance data can be calculated using relations like Equation 2 [27]. Apart from the calculation of frequency dependent immittance data, it is possible to count the resonance frequencies f_r of all slices with similar values. A bin size of 0.05 for the logarithm of the frequency and a total number of slices of 500 was chosen. Plotting the number of counts vs. frequency (Figure 4b)) then allows the unique probability to illustrate the distribution of relaxation frequencies and correlate it to the conductivity profile as well as to the imaginary part of the modulus.

Furthermore it is possible to determine frequency dependent immittance data for specific regions within the sample, such as the anode, bulk, or cathode regions. This is automatically achieved while the simulation is executed by comparing the actual oxygen vacancy concentration at a defined position $[V_o^{\bullet\bullet}](x)$ with the initial oxygen vacancy concentration $[V_o^{\bullet\bullet}]_{\text{initial}}$. This leads to the following conditions:

$$[V_o^{\bullet\bullet}](x) < [V_o^{\bullet\bullet}]_{\text{initial}} \quad \text{for anode,}$$

$$\left[V_o^{\bullet\bullet} \right](x) = \left[V_o^{\bullet\bullet} \right]_{\text{initial}} \quad \text{for bulk, and}$$

$$\left[V_o^{\bullet\bullet} \right](x) > \left[V_o^{\bullet\bullet} \right]_{\text{initial}} \quad \text{for cathode.}$$

The discrimination of the distinct regions is demonstrated in Figure 4 for the intermediate state and highlighted by different colors. This is particularly valuable for analysis since it is now possible to correlate different changes in slope or appearing shoulders of the $M''(f)$ spectrum to a distinct region of the sample or shape in distribution of relaxation times. In reverse it enables to make assumptions of the actual conductivity profile based on measured immittance data.

3.2.1. The initial, undegraded state

After clarifying the derivation and meaning of the different plots in Figure 4, the simulated data presented here will be discussed and related to the measured immittance data in Figure 3b). The simulation of the initial, undegraded state (dashed line) shows a homogeneous conductivity profile. As already discussed above, the simulated conductivity based on relations in literature [9,20] is in very good agreement with the measured value. Consequently, the measured and simulated modulus data $M''(f)$ characterized by one distinct maximum at 200 Hz match. As can be expected from the homogeneous conductivity profile, all 500 slices exhibit the same relaxation frequency leading to no distribution of relaxation frequencies.

3.2.2. The intermediate state

The condition of the intermediate state (straight line in Figure 4) was chosen in a way that the anode and cathode region have not yet met and are still separated by a bulk region. This condition appears to be similar to the measured conductivity profile by Rodewald *et al.* [3] However, the coloration front is at a different position within the crystal, which results from

different impurity, quenching, and degradation conditions [3,20]. The simulations shown here are adjusted to the impurity, quenching, and degradation conditions of the measured sample. To further verify this, an additional STO:Fe single crystal prepared under the same conditions was degraded with lateral electrodes. The resulting coloration is shown in the inset of Figure 4a) and matches the simulated ratio of anode to cathode widths.

According to the simulated oxygen vacancy profile, the data in Figure 4 is separated in anode, bulk, and cathode regions. Figure 4a) illustrates that the conductivities of both anode and cathode region increase during degradation, whereas the conductivity of the bulk region remains unaltered compared to the initial value. Thus the relaxation frequency of the slices in the bulk region is unchanged, but their number is decreased. Consequently, the magnitude of the $M''(f)$ spectrum related to the bulk region decreases. The correlation of the number of slices with the magnitude in the $M''(f)$ spectrum becomes apparent. While the distribution of relaxation frequencies is sharp for the bulk region, defined distributions arise for the anode and cathode region, which is in both cases related to a variation in conductivity. The distribution becomes broader with increasing variation in conductivity. It is noteworthy to mention that the distribution of relaxation times observed here is very asymmetric. Thus fitting of immittance data of degraded STO:Fe single crystals even with constant phase elements [27] – which can only describe a symmetric distribution of relaxation times – is not appropriate. By proving that both anode and cathode region exhibit an asymmetric distribution of relaxation frequencies it becomes apparent that the equivalent circuit used by Liu *et al.* [4] cannot describe the degraded state sufficiently. Thus, all derived conclusions

like polaron conduction within the cathode region may become limited to his specific conditions of the partial recovery state and not universal until further investigations are made. In addition, the identification of bulk, anode, and cathode can be performed based on the proportionality of the resonance frequency and the conductivity (Equation 5). Since the conductivity in the cathode region is higher than the one in the anode region and both are higher than the conductivity of the bulk region, the maxima of the $M''(f)$ spectra can be assigned as bulk, anode, and cathode with increasing frequency. Based on this comprehension the change in measured and simulated conductivity during the degradation process will be discussed with respect to each region.

The bulk region during degradation

Differences in bulk conductivity at the beginning of degradation are illustrated by arrows in Figure 3b) (measured data) and Figure 4c) (simulated data). While the maximum in $M''(f)$ shifts to higher frequencies, indicating that the conductivity of the bulk region increases, the simulated bulk conductivity does not change. The constant simulated bulk conductivity results from the assumption of local thermodynamic defect equilibria and quasi-neutrality [2,19]. Consequently, the electronic equilibration is due to generation and recombination and is assumed to happen on such a small time scale that electron and hole concentrations are only defined by the lateral distribution of defect states like oxygen vacancies and iron impurities, but not by drift or diffusion. Given the fact that the conductivity and thus the electric field is constant within the bulk region, the flux of oxygen vacancies into and out of each slice is equal as long as the considered slice is not in contact with the anode or cathode region. Consequently, the simulations do not allow the bulk conductivity to be altered.

However, the experimental results suggest that those assumptions are untenable. Since – as discussed above – the bulk conductivity is only altered during degradation, but not during recovery, it is most likely that the applied electric field allows both holes and electrons to drift in the direction of the bulk region to increase its conductivity.

An increased bulk conductivity with applied voltage could also be linked to altered oxygen vacancy migration barriers due to complexed oxygen vacancies [39]. Indeed for the STO:Fe it was shown that the $(\text{Fe}'_{\text{Ti}})-(\text{V}^{\bullet\bullet}_{\text{O}})$ complex and the migration of oxygen vacancies result in two different TSDC signals [36,37]. Furthermore, electron paramagnetic resonance measurements suggest that complexed oxygen vacancies might easily move with an applied DC voltage, and the complex is a distributed defect and not a ridge nearest neighbor interaction between the acceptor and oxygen vacancy in the case of STO:Fe [40].

The cathode region during degradation

According to the two maxima in Figure 3b) of the degraded state, the measured conductivity of the cathode region is roughly 40 times higher than that of the anode region. However, this is only true at the final state, since the maximum in $M''(f)$ related to the cathode region first appears at frequencies that are more than one order of magnitude lower. Only thereafter, it shifts continuously to higher frequencies until the steady state is reached. Initially, no relaxation peak is observed at high frequencies. Consequently, the conductivity in the cathode region is much lower at the beginning of the degradation. However, the presented model by Baiatu *et al.* [2,20] exhibits a very fast increase of conductivity within the cathode region, due to the assumption of local thermodynamic defect equilibria. This assumption leads to a maximum in the $M''(f)$ spectrum that immediately occurs at high frequencies. Since this is not

experimentally observed, the high electron concentration must be decreased somehow. One possibility is that electrons react with oxygen vacancies to form singly charged oxygen vacancies as discussed by Rodewald *et al.* [3] However, this would not explain the increase of conductivity with advancing time. Another possibility would be that the electrons drift from the cathode into the bulk region due to the applied electric field. Thus, both experimentally observed conditions would be met, meaning that the bulk conductivity is increased, while the cathode conductivity is decreased at the beginning of degradation.

The anode region during degradation

Since the bulk conductivity is increased at the beginning of the degradation it can be assumed that the frequency response of anode and bulk regions overlap. During degradation, no more than two distinct maxima are observed at the same time. Thus the change in properties in the anode region is difficult to analyze using the measured modulus data. However, the anode region is expected to be described well since this is the region that dominates the degradation behavior that Baiatu [2] matched. This is discussed in detail below using Figure 5 and Figure 6 as well as a comparison of the shape of the conductivity decay in the anode region.

3.2.3. The final degraded state

At last, Figure 4 includes simulations of the degraded state. The experimentally observed shape with two maxima in $M''(f)$ positioned considerably higher in frequency than the maximum related to the bulk region can be reproduced. In addition, the second maximum, which is correlated to the cathode region, exhibits a significantly higher magnitude which can be explained by a larger width of the cathode region. The spacing between the two maxima indicates that the electron conductivity in the cathode region is roughly 40 times higher than

the hole conductivity in the anode region. However, the experimentally given ratio is only reproduced by the simulation if the conductivity of the cathode region is assumed to be three to four orders of magnitude lower than what could be expected from calculated electron density and given electron mobility [2,9]. This is illustrated in Figure 5b) which compares $M''(f)$ spectra at the final, degraded state that are simulated using different values for the electron mobility. Here, the electron mobility of $0.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ corresponds to the value for a free electron given by Denk [9] and results in two maxima that are positioned several orders of magnitude too far apart. A change in electron mobility was used to emphasize the fact that changing either the charge carrier density [3] or the mobility of electrons both result in a reduction of the electron conductivity, and neither of them can be excluded as an origin yet. Furthermore, the conductivity profile of the degraded state as well as the effective conductivity as a function of degradation time are presented in Figure 5. It becomes evident that a change in electron mobility impacts only the electronic properties in the cathode region noticeably. Using Equation 12 the effective conductivity, which is proportional to the current density, is calculated.

$$\sigma_{\text{eff}} = \left(\sum_{i=1}^n \frac{1}{\sigma_i} \right)^{-1} \quad (12)$$

The simulated increase in effective conductivity appears to be independent of the assumed electron mobility and the resulting conductivity profile. Consequently, the anode region, which exhibits the lowest conductivities, dominates the resulting degradation behavior. This clarifies that Baiatu's [2] approach to compare the time dependent degradation behavior with simulations to confirm the accuracy of the introduced model is not sufficient. Important aspects that pertain the electronic properties cannot be covered. It will be necessary to

readjust the model based on the measured modulus data during degradation and recovery shown in Figure 3. During discussion of the degradation characteristic of intermediate states it became apparent that tracing the conductivity profile as a function of time must be understood as the key to reveal the processes that impact resistance degradation in addition to oxygen vacancy diffusion, which still remains the major cause. In this respect it is important to start with discrepancies of measured and simulated conductivity and modulus data at the beginning of the degradation. This necessity can also be derived using Figure 5, which illustrates the effects of a reduction of the conductivity in the cathode region. Due to the reduced conductivity, the electric field distribution must be different from that calculated by Baiatu *et al.* [2] leading to a different time dependent oxygen vacancy diffusion. Figure 5c) shows that with lower conductivity and thus increased electric field within the cathode region the variation of the conductivity in this region is increased. Increasing the conductivity first in the entire single crystal as observed experimentally, followed by smaller changes in conductivity in both anode and cathode regions will thus be expected to have an even higher impact on the electric field distribution. Thus, changing conditions at the beginning of the degradation might have a huge impact on the final degraded state.

In consideration of the fact that the electric field distribution during the degradation process cannot be reproduced correctly using Baiatu's [2] model, it cannot be expected that simulated and measured final degraded states match. In Figure 6, simulated (sim A) und measured $M''(f)$ spectra and conductivity profiles at the final degraded state are compared. Further data is added based on a devised conductivity profile (sim B) to support conclusions that can be drawn from the measurement. Particular attention needs to be paid to the frequency range of

the $M''(f)$ spectrum below the maximum correlated to the anode region. The measured data in this frequency range is characterized by a perfect slope of $S=1$, indicating that there are no slices within the degraded single crystal exhibiting a relaxation frequency lower than roughly 2 kHz. Consequently, there is no region within the single crystal that is characterized by a conductivity lower than $3 \times 10^{-7} \text{ S cm}^{-1}$. However, the simulation does show a deviation from the perfect slope of $S=1$ to lower values in the same range. This deviation can be understood in combination with the distribution of relaxation frequencies f_r shown in Figure 4b) and the conductivity profile. The simulated anode region exhibits an asymmetric distribution of f_r with a maximum at higher frequencies. Thus at lower frequencies shape of $M''(f)$ is altered due to the overlap of anode slices with different conductivity values. A direct connection exists between the shape of the distribution of f_r and the shape of the decay in conductivity with increasing distance from the electrode/anodic STO:Fe interface. In case the conductivity is high in most of the slices and only a few slices exhibit lower conductivity a change in slope S can be observed at lower frequencies. However, the measurement exhibits a perfect slope of $S=1$ at low frequencies. This leads to the assumption that the anode region consists of a low amount of slices with high conductivity, but a high amount of slices with lower conductivity. This shape is similar to the one measured by Rodewald [3] and also the one used for the devised conductivity profile (sim B) in Figure 6b). The corresponding $M''(f)$ spectrum clearly shows the same slope S in the low frequency range as the measured spectrum. It is important to note that the predicted conductivity profile of the degraded state based on the measurements is actually observed for the intermediate state using simulations (see Figure 4b)). However, there is a transition of the shape during the last period of the simulated

degradation process which might not appear using a future revised model exhibiting a different electric field distribution.

To further verify the predicted conductivity profile within the anode region it is also possible to fit the measured modulus data. A Differential Evolution/Particle Swarm Optimizer [41] was employed as the minimizer in a complex nonlinear least squares regression in order to fit a set of equivalent RC elements to measured modulus data. However, this method exhibits a lower accuracy and number of slices compared to the simulation of the conductivity profile. To fit the measured data, 8 parallel RC elements connected in series are chosen (compare equivalent circuit shown in the inset of Figure 4a)) and Equation 8 and 9 are used.

Since fitting does not give information about which conductivity corresponds to which position within the crystal, the resulting conductivity values are ordered with respect to the expected conductivity profile discussed above. In Figure 6a) the fitted conductivity profile is given as circles. This profile affirms the predicted shape of conductivity profile in the anode region. However, efforts like increasing measured data points as a function of frequency need to be carried out in order to increase accuracy and number of fitted slices. This will be presented in a following publication.

3.3. Summary of deviations from previous publications

The degradation process is governed by the interaction of oxygen diffusion, resulting change in hole (anode) and electron (cathode) conductivity, and electric field distribution [2]. However, measured $M''(f)$ spectra allow to show that the conductivity profile within the STO:Fe single crystals undergoes different changes compared to what is predicted from the simulations. This mainly led to the conclusion that the assumptions of local thermodynamic

equilibrium as well as quasi-neutrality cannot be completely valid. These assumptions and the new insights have been summarized in Table 1. In addition, publications dealing with the magnitude of electron conductivity in the cathode region and the conclusions drawn here are presented. The different approaches have been introduced, and it could be shown that in both cases degraded STO:Fe that was partly recovered was analyzed. Up to now there is no conclusive clarification which of the presented approaches describes the degraded cathode region correctly. It is believed that the in-situ measurements of the immittance during degradation will set the foundation to analyze this problem in more detail when performed at different temperatures. This will be addressed in a following paper.

4. Conclusions

For the first time, time resolved electrical measurements have been presented for degradation in STO:Fe single crystals that cover the impact of electronic and ionic properties within the entire sample (not only highly resistive anode part) and are carried out while the voltage is applied (fully degraded sample without partial recovery). It was emphasized that plotting the measured immittance data as the imaginary part of the modulus M'' vs. frequency is the best way to analyze the data. The presented data was first discussed with respect to the proportionality of the relaxation frequency f_r to the conductivity σ . It could be derived that the conductivity increases in the entire single crystal at the beginning of the degradation which is consistent with Raith *et al.* [6]. Only thereafter, the two different cathode and anode regions emerge with further increasing conductivity. Along with the conception of how to simulate $M''(f)$ spectra based on conductivity profiles obtained by the model presented by Baiatu [2]

the measurements were discussed. It could be clarified that the maxima $M''(f)$ during degradation and recovery can be attributed to the bulk, anode, and cathode region with increasing frequency. Furthermore, deviations from perfect slopes in $M''(f)$ could be correlated to a distribution in relaxation frequencies. It becomes evident that both anode and cathode region are characterized by a considerably asymmetric distribution of f_r due to the spatial variation in conductivity. Consequently, fitting of immittance data of degraded STO:Fe can only be performed using a multiplicity of parallel RC elements but not using constant phase elements which restrict the distribution of relaxation times to symmetric cases. The reason that the process of resistance degradation cannot be described sufficiently by comparing the current density vs. time characteristics [2] was emphasized by simulations with different electron mobility. While this variation impacts the conductivity profile in the cathode region as well as the second maximum in the $M''(f)$ data, the current density vs. time characteristics are unaffected. Here it became apparent that only the anode region influences the observed current density due to its dominant resistivity.

The detailed analysis of changes in the bulk, cathode, and anode region during degradation as well as the final, degraded state mainly concluded as follows. The assumptions that a local thermodynamic equilibrium and quasi-neutrality condition is given during the degradation process cannot be supported. Especially the increase in conductivity within the entire single crystal at the beginning of the degradation does not substantiate the assumptions made by Baiatu [2]. Furthermore it was argued that deviations of the simulations from measurement at the beginning of the degradation can have a major impact on the final degraded state since the electric field distribution evolves differently with time. This was highlighted by a comparison

of the conductivity distribution within the anode region. The transition of an initial fast decay of the conductivity with distance from the electrode and subsequent saturation (observed for intermediate simulated and all measured states) should not change to a saturation in conductivity at the vicinity of the electrode and a decrease in conductivity that is only observed close to the anode/cathode interface.

Based on the $M''(f)$ spectra the electron conductivity within the cathode region can be assumed to be roughly up to 40 times higher than the hole conductivity in the anode region. Thus immittance spectroscopy can support the conclusion drawn by Rodewald [3] and Liu [4] that the electron conductivity within the cathode region must be considerably lower than assumed by Baiatu [2] using only doubly charge oxygen vacancies and the free electron mobility [9]. However, it could be shown here that both analysis were not performed at the final, degraded but partially recovered state. Up to now there is no foundation to argue if the reduction of electron conductivity within the cathode region is caused by a reduced charge carrier density or mobility of the electrons or even both. However, it is believed that the here introduced evaluation of time resolved immittance data with applied DC voltage provides the basic concept to solve this problem. This will be addressed in subsequent papers investigating the temperature dependence of the final, degraded state as well as presenting a new model to match the degradation behavior at the beginning of the degradation.

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Appendix A. Supplementary Information

Supplementary information related to this article can be found at .

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Figure 1. DC voltage profile as a function of time t . During degradation and recovery, several frequency sweeps are performed to monitor the changes of properties within the STO:Fe single crystal.

Figure 2. a) Impedance Z^* and b) modulus M^* plotted in the complex plane for different stages of degradation. While the impedance plane shows a depressed semi-circle for the degraded state, the modulus data exhibits two distinct semi-circles. Arrows indicate increasing degradation duration.

Figure 3. Correlation of a) measured increase in current density during degradation with b) measured features in $M''(f)$. The $M''(f)$ spectrum performs a transition from one bulk feature (initial) to an anode and cathode feature at higher relaxation frequencies (degraded). The different frequency positions of the regions are marked together with c) changes in $M''(f)$ during the recovery process. Arrows indicate increasing duration of either degradation or recovery.

Figure 4. Relation of simulated a) spatially resolved conductivity profiles, b) distribution of relaxation times as well as c) the imaginary part of the modulus for the initial (1), intermediate (2) and degraded (3) state. The intermediate state is subdivided in features caused by the anode, bulk, and cathode region.

Figure 5. Comparison of simulated a) effective conductivity as function of time, b) imaginary modulus data, and c) local total conductivity for different values of the electron mobility. The mobility of a free electron at 210 °C is $\mu_{n,free} = 0.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [9]. b) and c) are plotted for the degraded state. The change in electron conductivity shown within the cathode region shown in c) can be observed in b) due to a shift of the maximum to lower frequencies with decreasing conductivity. While b) and c) differ crucially with variation of electron mobility, a) is the same demonstrating that degradation is vastly dominated by the properties of the anode region.

Figure 6. Comparison of a) conductivity profiles and b) imaginary modulus data for the degraded state. The simulated conductivity profiles of sim A and sim B were used to calculate the $M''(f)$ spectra whereas the measured $M''(f)$ spectrum was used to fit the conductivity profile. The fitted data is given as symbols whereas the straight line indicates the estimated profile. The shape of the conductivity profile and thus the slope in $M''(f)$ differ crucial for sim A in comparison with the measurement and sim B.

Table 1 Summary of strength and weaknesses of earlier publications dealing with resistance degradation in STO:Fe.

Author:	Strengths	Weakness
Baiatu [2]	• match of measured and simulated increase in current density • oxygen diffusion to cathode side identified as major cause for degradation	• increase in current density is not unique (it only covers the anode region as shown in Figure 5) and is not sufficient to verify the integrity of the presented model • major inconsistencies are: ○ electron conductivity in cathode region too high ○ increased bulk conductivity at the beginning of degradation cannot be covered, so that the model to calculate the electric field distribution is oversimplified ○ deviation in electric field distribution leads to similar but not equal final degraded state • the assumption of local thermodynamic equilibrium and quasi-neutrality has to be reevaluated
Rodewald [3]	• first to measure the conductivity profile within degraded STO:Fe electrically • too high electron conductivity addressed by suggesting a reduced electron density $V_o^{\bullet\bullet} + e' \rightarrow V_o^{\bullet}$	• to measure the conductivity profile with microcontacts the degradation voltage needs to be turned off, which allows recovery • the measured conductivity profile cannot be related to the final degraded, but a partially recovered state since a bulk region is observed (during recovery the bulk region is immediately observed as shown in Figure 3c))
Liu [4]	• first to use modulus data to analyze degraded STO:Fe • degraded STO:Fe cannot be described by simple RC elements • additional branch correlated with polaron conduction introduced • observed activation energy and electron energy loss spectroscopy (EELS) data support polaron assumption	• the modulus data is measured without an applied DC field, so that the degraded sample can recover • while determination of the activation energy it is not ascertained that the recovery state does not change while temperature is varied • activation energy of 0.1 eV related to small polaron and width space charge region by EELS might be coincidence • questionable since anode and cathode exhibit asymmetric distribution of f_r • determined anode and cathode width is too small, since partially recovered

Figure 1

Figure 3

Figure 4

Figure 5

Figure 6