

# Oscillatory kinetics at solid/solid phase boundaries in ionic crystals

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## Abstract

The transfer of matter and charge across interfaces between two solids is related to defect relaxation in the regions near the interface. A transfer rate which exceeds the rate of defect relaxation may lead to degradation of the interface, causing a feedback effect for the transfer process itself. As a consequence, non-linear phenomena (dissipative structures) like periodic oscillations of the interfacial properties can occur under conditions far from equilibrium. Possible mechanisms and experimental examples are discussed.

*Keywords:* Dissipative structures; Electrochemical oscillations; Interfaces; Ionic conductors; Point defects

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## 1. Introduction

The transfer of ions across boundaries between two solid materials plays an important role in solid-state reactions [1], in solid-state electrochemical devices [2] and in advanced ionic materials [3,4]. It is of basic interest for the understanding of solid-state kinetics [5,6]. An increasing number of theoretical and experimental studies, mainly driven by development of micro- and nanocrystalline materials, as also solid-state batteries and fuel cells, can be attributed to this strong interest (e.g. Refs. [7–21]).

The main aspect in most studies of ionic interface kinetics concerns the relation between an ionic flux across a boundary and the corresponding (electro) chemical driving force, i.e. the current/voltage characteristics (e.g. Refs. [7–9,11,16,17]). Thus,

experimental studies usually aim for the determination of the transfer resistance which a given boundary represents for the transfer of ions, and concepts which have been established in the description of solid/liquid interfaces (e.g. the Butler–Volmer equation) are transferred without serious discussion. Despite an increasing number of experimental studies, the corresponding knowledge is yet still restricted, due to many experimental problems. Most critical are the preparation of structurally and chemically well-defined interfaces which allow reproducible kinetic studies and the application of suitable local probes. The situation becomes even worse by the fact that, as yet, no experimental techniques exist for the direct local observation and analysis of solid/solid interfaces in situ [22]. Recently, microelectrodes with high spatial resolution have been applied in the study of grain boundaries in ionic conductors [23].

An additional and inherent problem in the experimental study of ion transfer across solid/solid

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boundaries, creating a major difference to electron transfer, is the possibility of both structural and morphological changes within the boundary region, driven by the transfer process itself [1,6]. The present paper focusses on these reactive aspects of ionic interface kinetics which complicate the study of ion transfer. It presents examples for non-linear kinetics observed in simple model systems, thereby emphasizing the importance of defect reactions and relaxation in boundary regions.

The paper is organized as follows: in Section 2 some general aspects of interface kinetics and possible instabilities are summarized. In Section 3 follows a short discussion of feedback mechanisms at inner boundaries, which may lead to strong non-linear or even oscillating kinetics. The electrochemical dissolution of a metal into a solid electrolyte (Section 4) and the electrolysis of a mixed conductor at an inert metal electrode (Section 5) are presented as two experimental examples visualizing a number of important aspects of ionic interface kinetics.

## 2. Interfacial instabilities

In order to present a more systematic picture, some general aspects related to non-equilibrium interfaces will be discussed in this section. The structure of a solid/solid interface may depend both on the intrinsic properties of the system under study and on its preparation. In general, coherent and semicoherent interfaces (e.g. low angle grain boundaries) are well defined and provide reproducible experimental model systems [13,24,25]. The coherent Ni/Ni<sub>2</sub>Si-interface which forms during the course of the reaction between Ni and Si provides an excellent example [13].

Most boundaries, however, which are of practical interest are incoherent, and the results of kinetics studies may depend also on the preparation of the boundary. As high angle grain boundaries (cf. nanocrystalline materials [26,27]), incoherent interfaces have to be considered as strongly disordered regions with high atomic mobility.

The focus of the present paper is directed toward non-linear and oscillatory kinetics at solid/solid interfaces. Non-equilibrium interfaces can be characterized in a rather general scheme by their velocity

relative to a given reference. We distinguish resting and moving boundaries. At resting boundaries, at least one of the two neighboring lattices remains intact and the transfer of ions does not lead to a shift of the boundary itself, i.e. transport processes in the neighboring phases supply and consume the transferring species. Typical examples for resting boundaries are provided by systems of the type AX/AY (AX, AY = cation conductors) or BX/CX (BX, CX = anion conductors). If either the electronic transference number of both phases equals zero or if the electronic flux is inhibited by suitable experimental means, the transfer of cations or anions is the only possible interfacial process. The system should remain stable even under non-equilibrium conditions, and time-independent transfer kinetics are observed.

Real systems always exhibit electronic conductivity, in its magnitude depending on the intrinsic band structure and the degree of doping. Strictly, ionic conductors have always to be considered as mixed conductors, with a more or less significant electronic contribution to the total conductivity. Real systems range from solid electrolytes with very low electronic conductivities (e.g. AgCl, AgI, CaF<sub>2</sub>) to mixed conductors with comparable partial ionic and electronic conductivities (e.g. Ag<sub>2</sub>S, CeO<sub>2</sub>) and semiconducting crystals with dominating electronic conductivity (e.g. CoO, NiO). Thus, a boundary between two ionic conductors always represents a region where not only the total conductivity changes, rather the transference numbers of ions and electrons, will also change, as emphasized by Schmalzried and co-workers [1,28,29]. If an electric current is drawn across such boundary by the use of reversible metal electrodes (in the case of cation conductors) or gas electrodes (in the case of anion conductors), this difference in charge transference may lead to 'internal' electrochemical reactions at the boundary ([1], pp. 226) (see Fig. 1a). One will observe the continuous decomposition of one phase at the boundary and the corresponding deposition of either the metal or the metalloid component. Corresponding experiments have been performed by Riess and Schmalzried [30] at boundaries of the type AgBr/AgCl, leading to the growth of metal dendrites within the boundary.

A situation which corresponds closely to the electrode processes at ion-blocking anodes (see

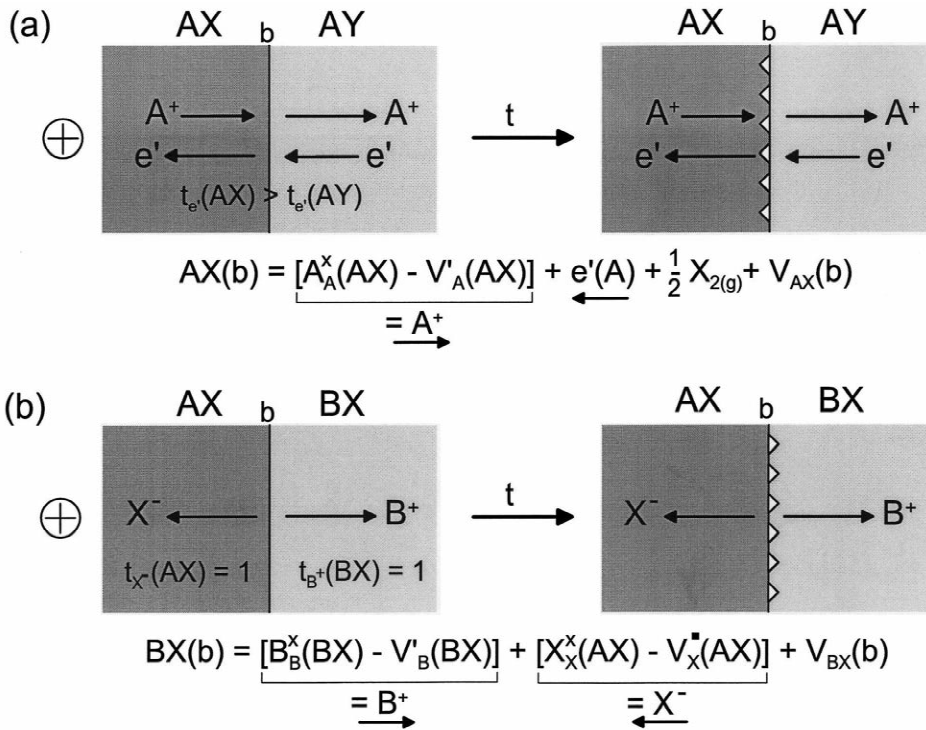


Fig. 1. Different basic experimental situations related to interfacial instabilities at resting boundaries: (a) ion transfer across a boundary AX/AY, (b) ion transfer across a boundary AX/BX.

below) is given if the non-metal potential is increased at the boundary under kinetic load (see Fig. 1a). In this case, the lattice of that electrolyte which contains the less oxidizing non-metal suffers from continuous decomposition, in its magnitude depending on the transport properties of both electrolytes, on the current load and on the rate of non-metal loss from the decomposition (boundary) region. The decomposition reduces the contact area of both phases by the formation of micropores (surface vacancies) and their aggregation and will give rise to strong non-linear kinetics, even at low current densities. Mechanical pressure which is exerted to the interface will have strong influence on the kinetics. So far, no experimental example for this particular kinetic effect has been reported.

If these reactive processes are suppressed at the boundary (e.g. due to a high degree of coherency) the chemical potential of the components of the electrolytes will change locally. Chemical potential gradients are established which compensate the

differing partial fluxes in both phases in the stationary state. If the transition between crystal regions with different transference numbers takes place in a single lattice ('coherent' transition), extremely high chemical potential gradients can be induced. As Virkar and co-workers [31,32] demonstrated in the case of zirconia, exhibiting a steep gradient in the electronic transference number produced by inhomogeneous doping, internal oxygen activities (pressures) can be induced by electric currents that lead to the complete destruction of the lattice.

A second group of resting solid/solid interfaces is provided by metal/electrolyte boundaries. Due to strong technological interest these have been investigated for many years [33–38]. From the kinetic point of view, metal/electrolyte boundaries can be distinguished by their degree of 'reversibility': reversible electrodes with low polarisation resistance are given by parent metal electrodes of the type A/AX or alloy electrodes (A,B)/AX. Blocking electrodes B/AX are composed of a virtually inert metal B and

an electrolyte. Intermediate cases are possible if the electrode metal is not inert against anodic dissolution. All electrodes are subject to dissolution or growth processes at sufficiently high electric potentials. At reversible electrodes the electrolyte lattice remains intact, and the metal phase is either dissolved anodically (see Fig. 2a) or grows cathodically. At ion-blocking electrodes, either the electrolyte is dissolved anodically (electrolysis, see Fig. 2b) or the metal component of the electrolyte is deposited cathodically. These processes generally lead to time-dependent behaviour of the interface, since its structure and morphology is changing continuously. In Section 4, examples of both reversible and blocking electrodes are presented which show that strong non-linear kinetics at electrodes is rather the usual case than an exception.

Still another situation at a resting interface is provided by the combination of two electrolytes which only allow charge transfer by the electrolysis of one electrolyte (see Fig. 1b). An example of such

system is well represented by the couple YSZ/CoO. If the semiconducting CoO is used as the cathode, it decomposes in order to produce oxygen ions which are then dragged across the YSZ toward the anode. The cobalt ions will move in the counter direction, leading to the dissolution of CoO at the boundary. If the CoO lattice is not dissolved layer by layer, one again expects structuring of the surface by the formation of surface vacancies and pores. A strong decrease of the contact area is the consequence, leading to an oscillating interface kinetics (C. Korte, personal communication).

Regarding Figs. 1 and 2, a number of different kinetic situations at interfaces can be realized which all lead to the dissolution (destruction) of one lattice. In the case of reversible and ion-blocking metal/electrolyte boundaries, electrochemical oscillations have already been observed. A study of the dissolution of one electrolyte lattice at an electrolyte/electrolyte interface has not yet been reported. The reverse case, i.e. the deposition of metal at an

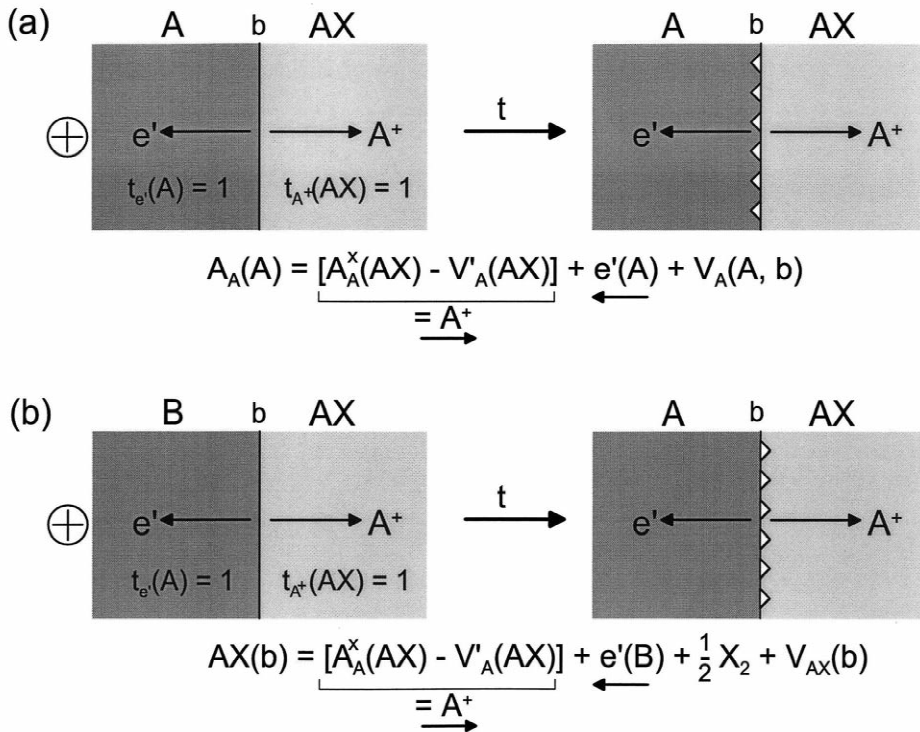


Fig. 2. Different basic experimental situations related to interfacial instabilities at resting electrodes: (a) ion transfer across a reversible electrode A/AX; (b) electrolysis at an ion-blocking electrode B/AX.

electrolyte/electrolyte interface, has been investigated by Riess and Schmalzried [30].

Moving boundaries require the simultaneous growth of one phase and annihilation of the second phase. Typical examples can be found in crystals which undergo a phase transition. Schmalzried and co-workers studied the phase transition between the  $\alpha$ - and  $\beta$ -phases of silver sulfide and silver selenide, which induces characteristic chemical potential oscillations if the  $\alpha/\beta$ -boundary is moving through the crystal [15,39]. An important macroscopic aspect of moving boundaries is the question whether a boundary moves in a morphologically stable manner, or whether it becomes morphologically unstable. A number of theoretical and experimental studies on the problem of morphological stability have been reported by Schmalzried ([1], p. 11) and Martin and co-workers [40,41]. In many cases, relatively simple rules can be applied in order to decide whether a moving boundary will remain stable or will become unstable. The morphology of an unstable boundary itself, however, can usually not be predicted by simple arguments. Rather computer simulations [42] or sophisticated theoretical arguments have to be applied [43].

An example for a morphologically unstable boundary is depicted in Fig. 3. If YSZ is polarized cathodically with a platinum electrode, the reduction advances with an unstable front through the crystal starting from the cathode. Corresponding experiments and more details can be found in Ref. [44].

Clearly, internal electrochemical reactions and related instabilities can also occur at moving boundaries. Yet no examples have been reported.

### 3. Feedback mechanisms

The occurrence of oscillatory electrochemical reactions, as one example of dissipative structures, requires at least one positive feedback step in the kinetics [45–47]. For chemical oscillators, Franck analysed different cases of positive and negative feedback and defined the principle of a so-called antagonistic feedback [46]. Simply speaking, any oscillating system contains both de-stabilizing positive feedback steps and stabilizing negative feedback steps. So far, a number of different feedback mecha-

nisms have been exemplified in various oscillating systems. Thus, the strong non-linear voltage dependence of an electric resistance, a membrane resistance or the tunnel effect may provide a feedback step. Other typical cases are feedback steps based on the temperature dependence of rate constants or on the concentration dependence of heterogeneous catalysis. During recent years, the study of related dissipative structures has found enormous theoretical and practical interest, and a number of excellent books and reviews are available (e.g. Refs. [48,49]).

Dealing with the kinetics of solid/solid interfaces, the question of possible feedback mechanisms as possible causes for the occurrence of oscillatory kinetics arises. To date only a few experimental examples for oscillatory kinetics in solid-state systems have been investigated (e.g. Refs. [50–55]), and the understanding of the underlying mechanisms is generally poor. Well known examples of oscillatory behaviour—at least from a phenomenological point of view—are the formation of multilayered reaction products during high-temperature oxidation (e.g. of Ti–Zr alloys) based on a thermal feedback [50], the formation of layered tarnishing films during high-temperature corrosion of titanium based on a mechanical (elastic) feedback [51,52], and chemical potential oscillations during the phase transformation of certain non-stoichiometric phases [15,39,56]. The feedback mechanism of the latter phenomenon has not yet been definitely identified. Our own experiments on the anodic dissolution of metal electrodes and the electrolysis of solid electrolytes, as depicted schematically in Figs. 1 and 2, provide additional examples for a mechanical feedback caused by the accumulation, i.e. the slow relaxation, of lattice defects at a boundary.

Often found in many chemical oscillators is thermal feedback by the evolution of reaction heat. An example for such thermal feedback in a solid-state reaction is provided by the oxidation of Ti/Zr alloys in oxygen atmosphere [50]. If the oxidation is run within a definite temperature range, the reaction leads to a layered product consisting of two different phases. The surface temperature of the oxidizing specimen oscillates simultaneously with the growth process. Generally, thermal feedback will be less important in inorganic solid-state kinetics than in molecular chemistry. Most inorganic solid-state re-

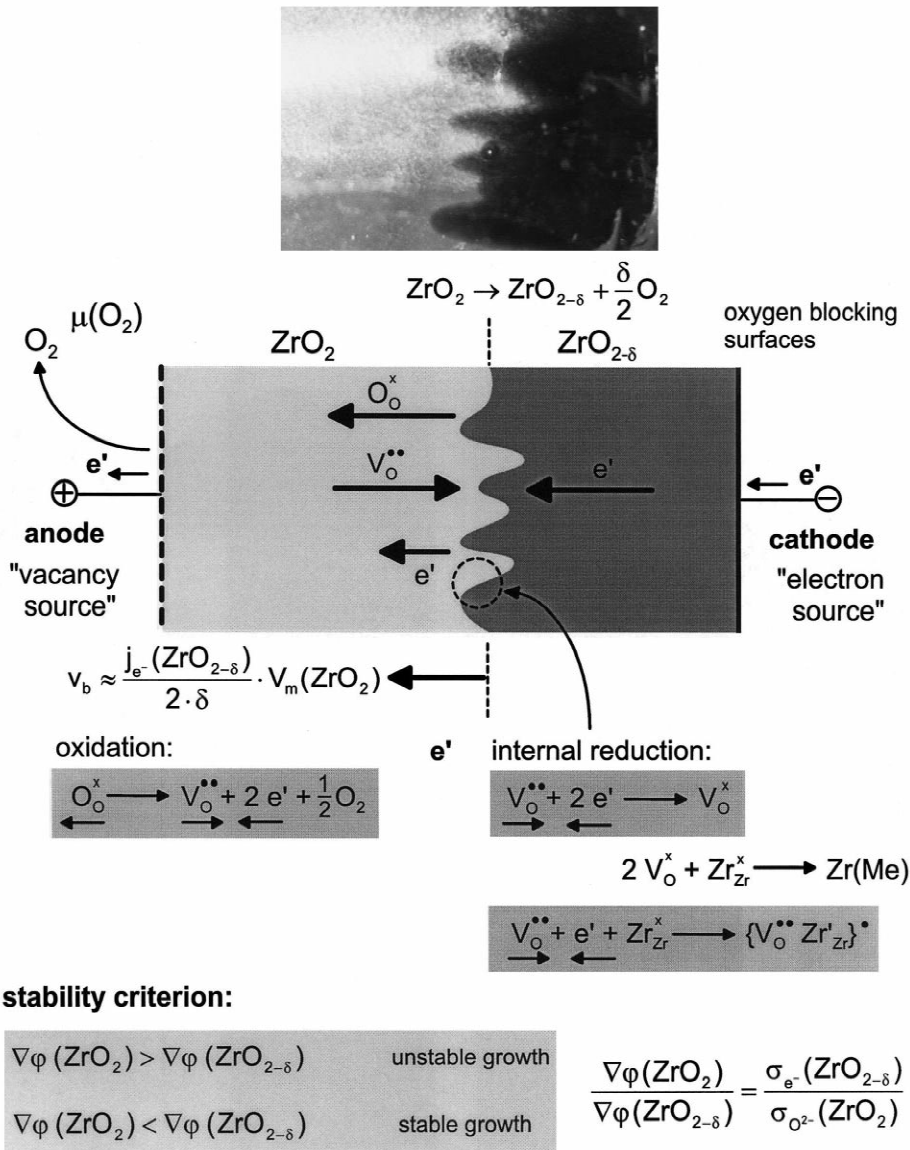


Fig. 3. Processes at the moving internal reduction front in YSZ. The top figure shows a photograph of a reduction front in single crystalline YSZ [44]. The bottom box notes the stability criterion for the moving boundary ( $\varphi$  = electric potential).

actions require high temperatures in order to obtain sufficiently high reaction rates (transport coefficients), and thus, enthalpic effects become less important.

In the solid state mechanical effects are much more important, i.e. interaction by elastic distortions of a lattice and plastic deformation by the generation

and motion of dislocations. Coherent and semicoherent interfaces induce elastic distortions in the neighboring lattice regions, which influence local defect equilibria. Pierraggi and Rapp discuss the Ni dissolution at the inner (resting) interface Ni/NiO during high-temperature corrosion of nickel by the model of an semicoherent interface. As an explanation for the

strong adhesion of the growing oxide film to the metal substrate, despite the formation of metal vacancies during the oxidation process, they suggest periodic dislocation climbing as a possible mechanism for the complete relaxation of metal vacancies (cf. metal dissolution in Section 4) [25]. In the oxidation of titanium which leads to an inward growth of  $\text{TiO}_2$ , a periodic rupture of the oxide film from the metal substrate is observed [51,52]. Under suitable experimental conditions one observes the periodic growth of hundreds of similar appearing oxide layers (thickness of approximately  $1 \mu\text{m}$ ) (see Fig. 4). Detailed experiments show that relatively thin titania films (less than  $1 \mu\text{m}$ ) still adhere to the substrate. With increasing thickness the film starts to peel off locally, and finally the contact breaks completely. Obviously, only thin titania films allow a sufficient relaxation of the elastic distortion which is induced by the lattice mismatch at the boundary. If a critical thickness is approached, the relaxation of the elastic stress is not efficient enough and the contact of both phases breaks.

Low frequent oscillations (time period in the order of 60 s) of the chemical potential of silver metal have been observed during the spatially controlled phase transformations  $\beta\text{-Ag}_2\text{S} \rightleftharpoons \alpha\text{-Ag}_2\text{S}$  [15,56] and  $\beta\text{-Ag}_2\text{Se} \rightleftharpoons \alpha\text{-Ag}_2\text{Se}$  [57]. A suitable temperature dif-

ference across the sample includes the transformation temperature, and an inhomogeneous crystal with a well-defined interface is thereby obtained. By shifting the temperature gradient along the sample, the phase boundary is driven along it and leaves the transformed crystal behind the moving boundary. Since the silver excess in both phases differs by orders of magnitude, the boundary has to act as a source or sink for the silver component. Chemical diffusion is thus induced. If the chemical potential of silver metal is measured at fixed positions along the sample, characteristic oscillations of the potential are observed. Schmalzried and co-workers discuss three different mechanisms for the observed chemical oscillations: (a) non-linear coupling of different defect relaxation and transport steps at the boundary (see comment below); (b) discontinuous boundary motion by the periodic rupture of dislocation networks from the semicoherent interface; and (c) discontinuous boundary drag by impurities. For more details, the reader is referred to Refs. [15,56,57].

Finally, the possible occurrence of chemical or electrochemical oscillators on the basis of coupled point defect reactions at boundaries, as proposed in Ref. [1] (p. 254), shall be discussed briefly. Schmalzried suggests that the coupling of both non-linear transfer and relaxation steps of point defects together with transport processes in the neighboring phases may lead to oscillatory kinetics, even at the interface between two different ionic conductors with simple Frenkel disorder. So far, no quantitative formal treatment or experimental study supports that idea. Rather one has to realize that the main difference between typical chemical oscillators and possible solid-state oscillators bases on the fact that molecular reactions allow autocatalytic steps (non-systemic positive feedback [46]). Considering point defect kinetics, no equivalent type of an autocatalytic reaction appears to be possible. Rather site conservation in the crystalline state prevents autocatalytic steps. Thus, one major source of positive feedback is generally missing in the solid state. However, if atom transfer across a solid/solid boundary is related to the dissolution of a lattice, i.e. to the creation of spatial interface (surface) instabilities (vacancies and pores), positive feedback becomes possible, as outlined above and as exemplified below.

In conclusion, we have to expect other feedback

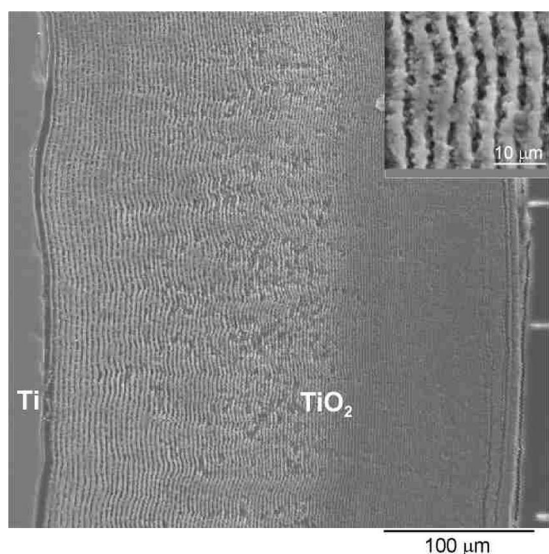


Fig. 4. SEM picture (cross-section) of the reaction product of titanium oxidation ( $T = 900^\circ\text{C}$ ,  $a(\text{O}_2) = 0.01$ ,  $t = 24 \text{ h}$ ).

mechanisms in solid-state kinetics than in fluid-phase kinetics. At coherent and semicoherent boundaries we expect an influence of elastic effects, and we have to take the motion of dislocations and their interaction with point defects into account. As a consequence of slow defect relaxation, non-equilibrium boundaries may accumulate point defects and thus may suffer from serious structural and morphological changes. In the next two sections, corresponding experimental observations are summarized.

#### 4. The anodic dissolution of a metal into a solid electrolyte

The anodic dissolution of a metal A into a cation-conducting compound AX represents an important kinetic step during the deloading of solid-state batteries and during high-temperature corrosion. Therefore, the kinetics of metal dissolution has been investigated for many years. Primarily, interfaces of the type Ag/AgX<sub>v</sub> (X = Cl, Br, I, S, Se) have been studied due to the stability of the silver ion-conducting compounds and their high ionic conductivity [5,7,9,19,21,33–38].

As discussed above, a virtually reversible metal electrode may be subject to kinetic degradation by the accumulation of metal vacancies and the creation of pores. In Fig. 5, the experimental setup together with a schematic picture of the microscopic processes at the anodic boundary are shown, assuming an unrealistically proper (coherent) boundary at this point. According to the reaction equation in Fig. 2a, metal vacancies are formed in the metal (on the metal surface) during the transfer of ions into the electrolyte. Correspondingly, the transferring ions occupy vacant sites in the electrolyte lattice. Thus, the transfer process in total, as suggested in Fig. 5, comprises at least three different steps: (a) the formation and relaxation of a vacancy on the metal surface; (b) the jump of the ionized metal atom into the electrolyte lattice; and (c) the relaxation of the new ion in the electrolyte lattice. If we assume that all ionic relaxation and transport steps in the solid electrolyte occur sufficiently fast, it is the relaxation of vacancies in the metal which controls the interface kinetics.

If we assume that the relaxation of metal vac-

ancies proceeds by bulk diffusion into the metal electrode, we estimate an anodic limiting current density of a silver electrode of approximately 50  $\mu\text{A}/\text{cm}^2$  at  $T = 800^\circ\text{C}$  [6]. Typical current densities in anodic dissolution experiments at much lower temperatures are in the order of 1  $\text{mA}/\text{cm}^2$ , and thus, bulk diffusion of vacancies will definitely not be able to provide a sufficiently high relaxation rate.

As a consequence of the slow relaxation of metal vacancies, the vacancies accumulate and form pores at the boundary. The formation of pores has been proven indirectly by dilatometric measurements in situ (cf. Ref. [38]). In Fig. 6, the results of an experiment at the interface Ag/AgI are depicted. The anodic overvoltage (see Fig. 6a) oscillates periodically with a rather low frequency. Simultaneously, the length change of the anode/electrolyte couple shows step-like oscillations with an identical frequency. If one assumes that (in a first-order approximation) the formation of vacancies in the boundary and their accumulation to pores produces no measurable length change, the oscillatory dilatometer signal can be interpreted as a consequence of alternating pore growth and annihilation. In Fig. 6c, the corresponding pore volume normalized by the geometric interface area ( $V_p/A$ ) is shown as a function of time. ( $V_p/A$ ) has the dimension of a length and can be interpreted as the thickness of a porous boundary region produced kinetically during the dissolution process. The zero pore volume at  $t = 0$  represents an arbitrary value, since the pore volume in the beginning of the experiment is not known. Only the change in pore volume can be determined from the experiment. However, from the analysis of an initial transient in the dilatometer signal one can estimate an initial thickness of the porous region in the order of 10  $\mu\text{m}$ . Fig. 6 shows that this thickness oscillates with an amplitude of less than 1  $\mu\text{m}$ . Thus, during anodic dissolution, a porous boundary region is formed which exhibits slight oscillations of its width in the order of 10%.

The picture is complicated by the fact that at least three different transfer processes can be distinguished in dynamic voltammograms (see Fig. 7b). Characteristic maxima indicate these individual transfer steps which occur at different overvoltages. Thus, process (a) takes place at relatively low overvoltages in the order of a few mV and is



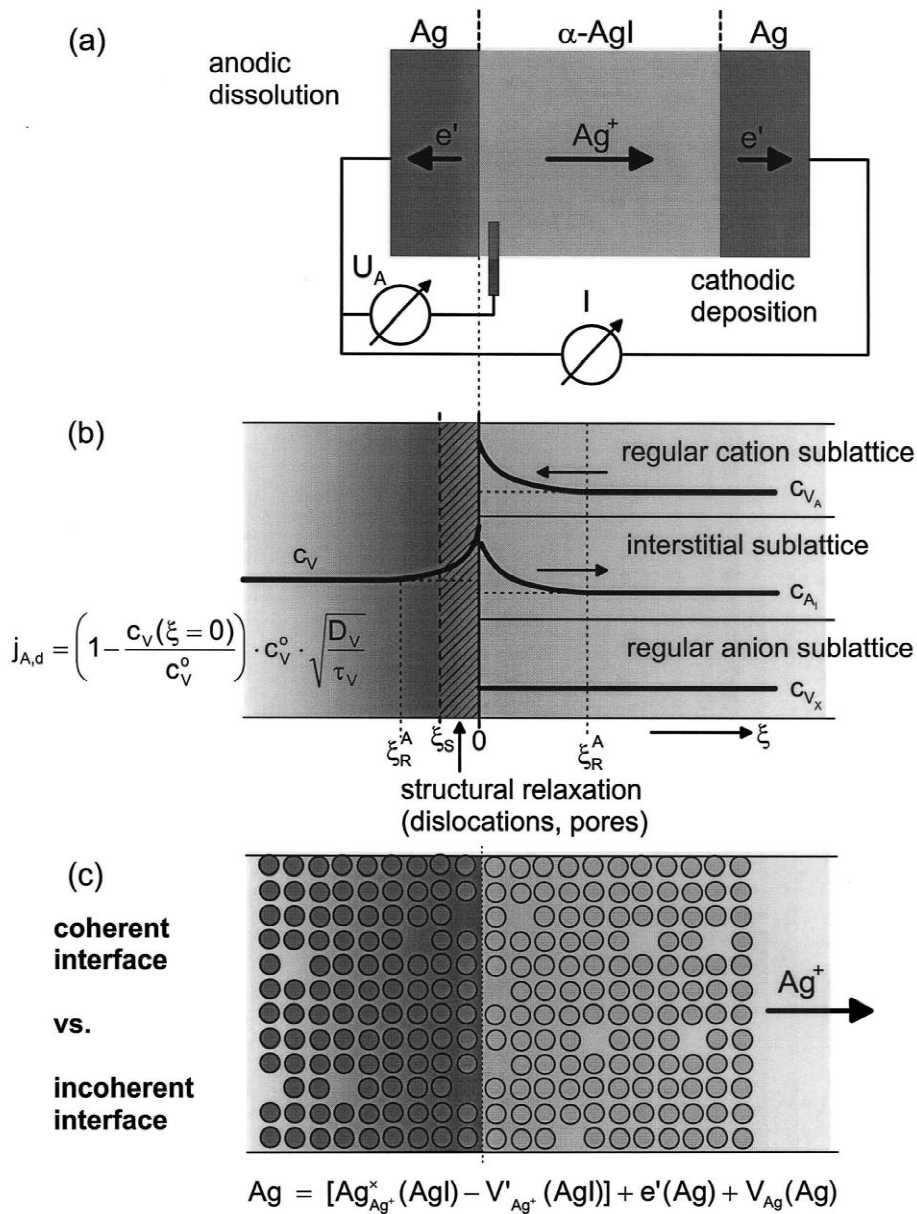


Fig. 5. General scheme of processes at a metal/solid electrolyte boundary: (a) schematic experimental setup, (b) defect relaxation, (c) schematic and simplified representation of the microscopic situation.

responsible for the base line in the galvanostatic time series. Process (b) takes place at overvoltages of approximately 50 mV and is responsible for the small shoulder in the galvanostatic voltage peaks. Process (c) requires relatively high overvoltages in the order

of some 100 mV and corresponds to the broad maxima of the galvanostatic time series which are superposed by high-frequency oscillations with small amplitude.

Since no analytic tools for a direct local study of

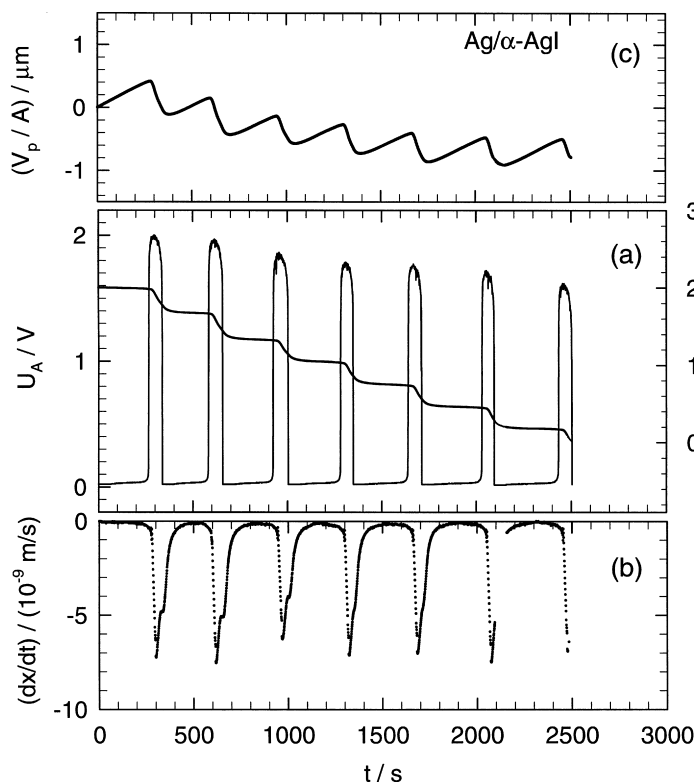


Fig. 6. Anodic galvanostatic dissolution of Ag at an Ag/AgI-electrode ( $T = 260^{\circ}\text{C}$ ): (a) overvoltage and the corresponding dilatometer signal (step-like line) as a function of time; (b) rate of length change of the Ag/AgI-couple; (c) pore volume in the interface region normalized by the geometric interface area as a function of time (see Ref. [38] for details).

the interfacial processes are available, the identification of these individual transfer steps is difficult. However, process (a) is probably related to the metal dissolution at small interface areas with very high exchange current densities. Comparable high exchange current densities are observed in the study of metal whisker/electrolyte interfaces and might be caused by a virtually coherent contact around a screw dislocation in the metal surface. Thus, process (a) gives some indication of locally restricted coherent contacts at the interface. Process (c) shows the characteristic features of oscillations during the electrolysis of solid electrolytes, thus it might be related to the decomposition of AgI and corresponding pore formation in the electrolyte surface. Process (b), which takes place at intermediate overvoltages, might be due to the transfer of silver adatoms. These are supplied by surface diffusion on the surfaces of pores and probably play a crucial role

in the formation of the porous structure during the dissolution process.

Summarizing, a number of individual processes take place simultaneously and are coupled through the complicated porous structure of the boundary region to each other. The transfer itself causes the porosity and, thus, a complicated network of feedback steps is set up. The mechanical pressure orthonormal to the interface plays the role of a control parameter [21]. Its strong influence on the kinetics gives additional evidence for the macroscopic character of the interfacial instabilities. In terms of Franck's analysis, both systemic and non-systemic feedback steps are involved. A systematic physico-chemical model of the oscillatory kinetics still has to be developed.

Electrochemical oscillations have also been observed at ion-blocking interfaces (anodic polarisation) of the type Pt/AgX ( $X = \text{Cl}, \text{Br}, \text{I}$ ) [5,57] and

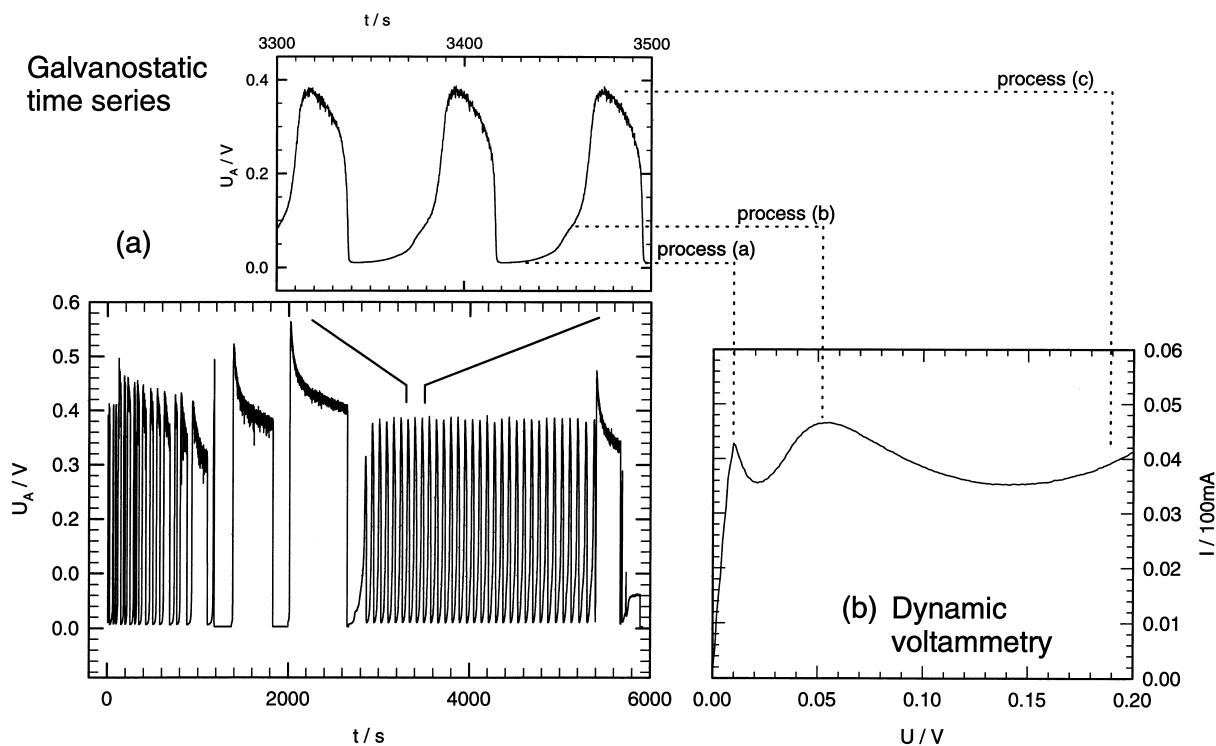


Fig. 7. Anodic galvanostatic dissolution of Ag at an Ag/AgI-electrode ( $T = 260^{\circ}\text{C}$ ,  $I = 1.56 \text{ mA/cm}^2$ ): (a) overvoltage as a function of time; (b) dynamic current/voltage characteristics of the electrode from a cyclic voltammogram (sweep rate,  $0.1 \text{ V/min}$ ).

Pt/Ag<sub>4</sub>RbI<sub>5</sub> [58]. So far, no oscillations with well-defined modes have been observed in these systems. As depicted schematically in Fig. 8, the galvanostatic voltage oscillations are caused by the local decomposition of the electrolyte and the corresponding pore formation. Thus, again a mechanical feedback is operating.

## 5. The anodic electrolysis of an ionic conductor

The anodic electrolysis of a cation-conducting solid electrolyte at an inert electrode leads to the annihilation of negatively charged vacancies, which migrate toward the anode driven by the electric field, and to the oxidation of the non-metal anions. The corresponding reaction equation is shown in Fig. 2b. Each non-metal molecule which is formed leaves two vacant lattice molecule sites at the boundary, i. e. the contact area is continuously reduced during the electrolysis. In Fig. 8, the electrolysis of semicon-

ducting Co<sub>1- $\delta$</sub> O at a platinum point electrode is depicted schematically. Co<sub>1- $\delta$</sub> O contains mobile cation vacancies which are negatively charged relative to the cation sublattice, but due to a small ionic transference number in the order of  $10^{-4}$ , the electric current is primarily maintained by electronic charge carriers (electron holes). Applying a constant current of  $1 \text{ mA}$  to the electrode with a geometric contact area of  $100 \mu\text{m}^2$ , the oxide is thus dissolved with a relatively large rate of approximately  $0.1 \mu\text{m/s}$ . As already reported in Ref. [37], quasi-periodic oscillations of the anodic overvoltage with a frequency of roughly  $0.5 \text{ s}^{-1}$  are observed, being equivalent to the annihilation of approximately  $0.2 \mu\text{m}$  oxide per oscillation period. This length is in surprisingly good correspondence to the typical length per oscillation period, which has been observed at Ag/AgI-electrodes. It shows that the oscillatory kinetics is rather caused by macroscopic morphological changes than by structural changes on an atomic scale.

Fig. 9 shows the result of a typical galvanostatic

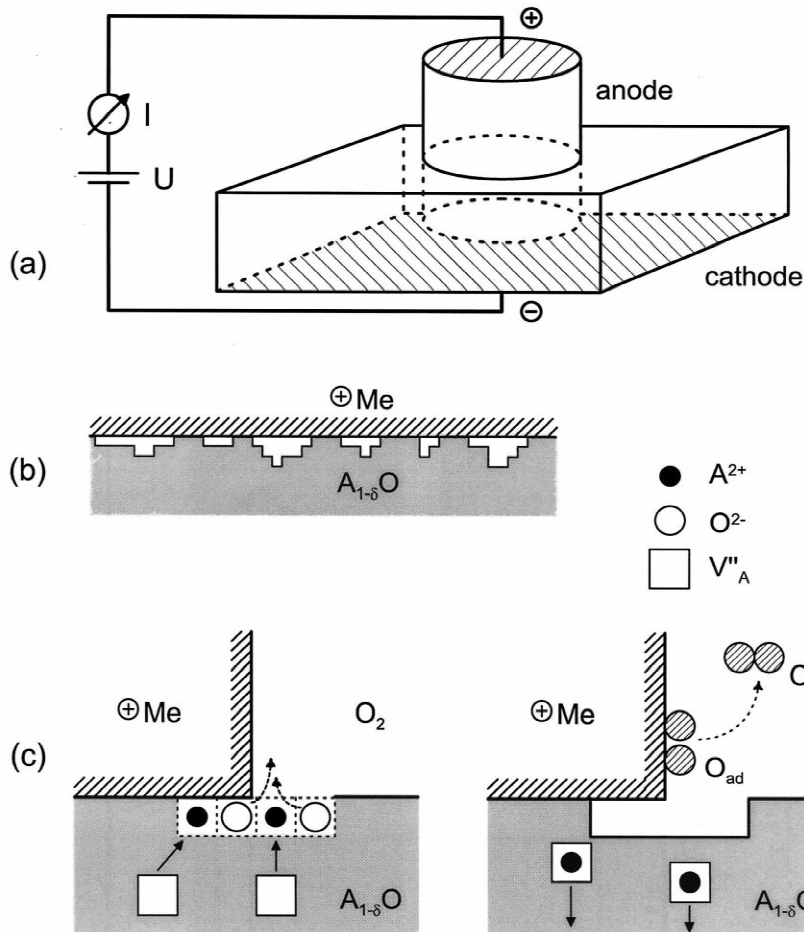


Fig. 8. Electrolysis of a semiconducting oxide  $\text{A}_{1-\delta}\text{O}$  at an inert metal (point) electrode. (b) Interfacial morphology, (c) anodic electrode process and formation of surface defects.

experiment. Experiments on the dissolution and growth of  $\text{CoO}$  and other oxides at YSZ anodes will be performed in a forthcoming study, in order to realize the kinetic situation which is depicted schematically in Fig. 1b. The build-up of high oxygen pressures in closed pores within the boundary is avoided by the use of an oxygen ion-conducting anode, and it will be interesting whether oscillatory kinetics is observed.

## 6. Conclusions

It is demonstrated that ion transfer across a solid/solid boundary is often related to reactive processes which may cause strong non-linear effects. As

exemplified by electrodes of the type  $\text{Ag}/\text{AgX}$  and  $\text{Pt}/\text{CoO}$ , these reactive processes will generally lead to morphological changes of the boundary and the surrounding region. These morphological changes cause mechanical instabilities and may lead to the complete destruction of initially well-defined boundaries. Furthermore, the ion transfer induces a strong feedback via the structural and morphological consequences of the transfer process.

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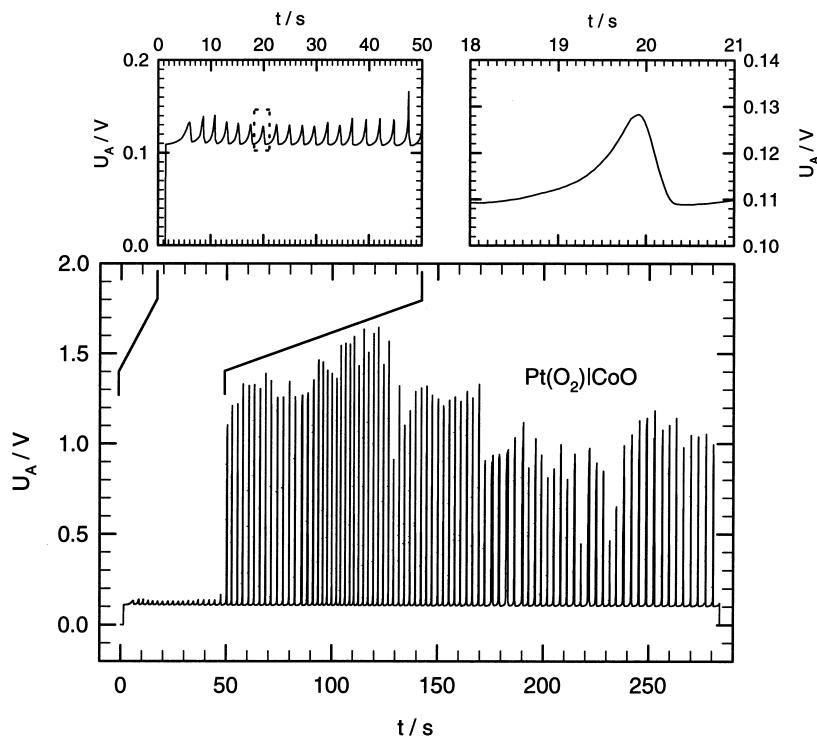


Fig. 9. Electrochemical oscillations at the anodic interface Pt/CoO: voltage  $U_A$  across the interface during galvanostatic dissolution of CoO ( $T = 1100^\circ\text{C}$ ,  $a(\text{O}_2) = 0.21$ ,  $I = 8 \text{ mA}$ ).

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