Julia Linnemann, Christian Leppin

The catalyst that stores charge first

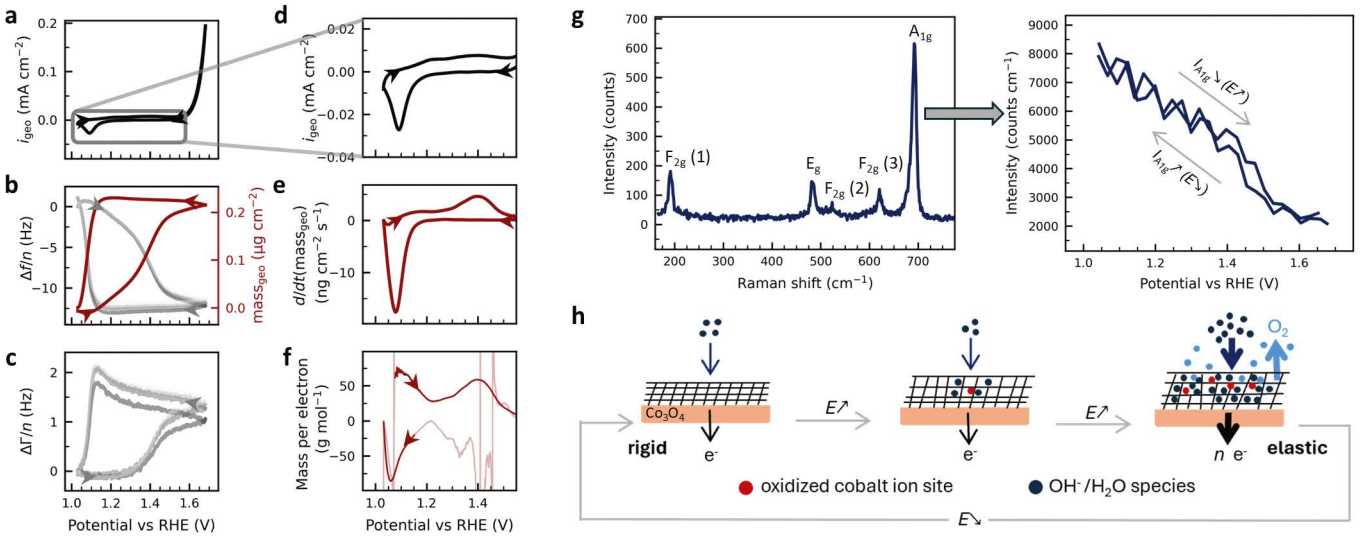

Fig. 1: Pseudocapacitive transformation of the near-surface Co_3O_4/electrolyte region. a) Cyclic voltammogram of a Co_3O_4 nanoparticle electrode in aq. 0.1 M KOH, b) simultaneous EQCM-D frequency response and corresponding mass change, and c) half-bandwidth shifts reflecting changes in interfacial softness. d–f) Enlarged pre-OER potential region showing d) geometric current density, e) time derivative of the mass trace and f) mass per transferred electron. The combined response resolves two anodic transformation regimes before the apparent OER onset: an initially rigid interfacial region that takes up several OH^-/H_2O species per oxidized cobalt cation site, followed by further electrolyte uptake accompanied by softening. g) *Operando* Raman spectra and potential-dependent integrated A_{1g} peak intensity indicating changes in the crystalline Co_3O_4 contribution during anodic polarization. h) Schematic summary. Panels adapted from Leppin *et al.* [1], licensed under CC BY 4.0.

Electrocatalysts have often been thought of as surfaces that provide active sites for a reaction. In this static picture, catalytic activity is governed by how strongly reaction intermediates bind to these sites and how readily the elementary electron-transfer and bond-forming steps proceed. This view has been highly productive: it allows materials to be compared by Tafel slopes, overpotentials, and descriptors. As a result, it has shaped much of the design language of modern electrocatalysis. Yet, for many oxide catalysts during the oxygen evolution reaction (OER), it is also incomplete.

Cobalt spinel, Co_3O_4, is a particularly instructive example. If an anodic potential is applied in aqueous alkaline electrolyte, the cobalt spinel is not simply a rigid surface on which OER intermediates adsorb and react. Instead, the near-surface region of Co_3O_4 pseudocapacitively stores charge through oxidation of cobalt ion sites, takes up several OH^-/H_2O species per transferred electron, changes its mechanical properties, and transforms into an oxyhydroxide-like layer (Fig. 1h) [1]. These changes begin before the macroscopic OER current dominates the voltammetric response.

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DOI-Nr.: 10.26125/6g4p-8386

This observation raises a central mechanistic question: do such pre-OER transformations merely form the active state of the catalyst, or do they expose interfacial processes that also occur repeatedly during catalytic operation? At potentials below the apparent OER onset, oxidation of cobalt ion sites is observed as pseudocapacitive contributions to the current. During sustained oxygen evolution at more anodic potentials, the catalyst may continue to cycle through related cobalt oxidation states during oxygen formation and release, so that the working interface is regenerated for the next turnover. In this sense, the electrochemically transforming oxide may be viewed as a redox-active catalytic interface. Similar to molecular redox catalysts, a fraction of metal ion sites can cycle between oxidation states during turnover. In an oxide, however, this redox cycling is embedded in an extended solid/electrolyte interfacial region. We call this ability of a subset of sites within the interfacial region to pass reversibly through catalytically relevant redox states under applied potential, without repeated conversion of the surface into a distinct stoichiometric phase, transformation lability [2]. The term describes how readily the working interface can reach and recover catalytically relevant redox states under electrochemical operation, and how effectively it avoids being trapped in less-active or degraded states.

This adds a second kinetic layer to the usual discussion of electrocatalytic OER at metal oxides. Besides the kinetics of hydroxide conversion at the electrolyte side of the interface, the kinetics of catalyst-state changes within the catalytic

cycle itself may become relevant. The apparent OER response is therefore only the outer layer of an electrocatalytic Matryoshka: inside it lies the electrochemical kinetics of cobalt-site conversion. Co_3O_4 thus behaves less like a static surface and more like a redox-active interfacial region that stores oxidative equivalents before and during oxygen evolution. To investigate this picture, interfacial changes must first be observed under electrochemical operation. Some of them may be part of the catalytic cycle, others may stabilize, modify, or merely accompany the working interface. *Operando* methods and carefully designed electrochemical experiments are therefore needed to follow these transformations and to identify which of them are catalytically relevant.

A first view into this working interface is provided by fast electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) [3, 4]. The method follows the mechanical resonance of a quartz crystal during electrochemical operation and is therefore sensitive to mass changes and viscoelastic changes at the electrode interface. In the Co_3O_4 study discussed here, this was combined with *operando* Raman spectroscopy to follow the catalyst during anodic polarization (Fig. 1) [1].

Two transformation regimes appear before the apparent OER onset. In the first regime, cobalt oxidation is accompanied by the uptake of several OH^-/H_2O species per transferred electron, while the interface remains mechanically rigid. In the second regime, further electrolyte uptake is accompanied by an increase in softness. The simultaneous mass and softness response suggests that the near-surface region does not simply bind individual adsorbates, but becomes a hydrous, more compliant interfacial region. Raman spectroscopy supports this interpretation: the crystalline Co_3O_4 contribution decreases during anodic polarization, consistent with partial amorphization of the near-surface oxide.

A key result of this study is that electrolyte uptake and interfacial softening should not be equated too directly with OER turnover. After prolonged polarization in the OER regime, the mass and softness hysteresis in the pre-OER region is strongly reduced, whereas the OER activity remains essentially unchanged. Thus, a large part of the incorporated electrolyte species appears not to participate directly in oxygen evolution. Some interfacial changes may be necessary to form or stabilize the working interface, while others may merely accompany operation.

The chemical meaning of the stored charge can be addressed by *operando* UV/Vis spectroscopy. For Co_3O_4 nanoparticle films, the absorbance at approximately 600 nm tracks the formation of Co^{3+} sites from Co^{2+} during pre-OER polarization [5]. Particularly instructive are open circuit potential (OCP)-decay experiments after polarization in the OER regime (Fig. 2c). In these experiments, the absorbance initially increases although the OCP already decreases. Thus, Co^{3+} sites are still formed while the electrode relaxes to lower potentials. This behaviour is best explained by self-discharge of Co^{4+} sites present during OER, where reduction of Co^{4+} forms additional Co^{3+} sites. The OCP decay therefore provides evidence that Co^{4+} states are reached under oxygen-evolving conditions.

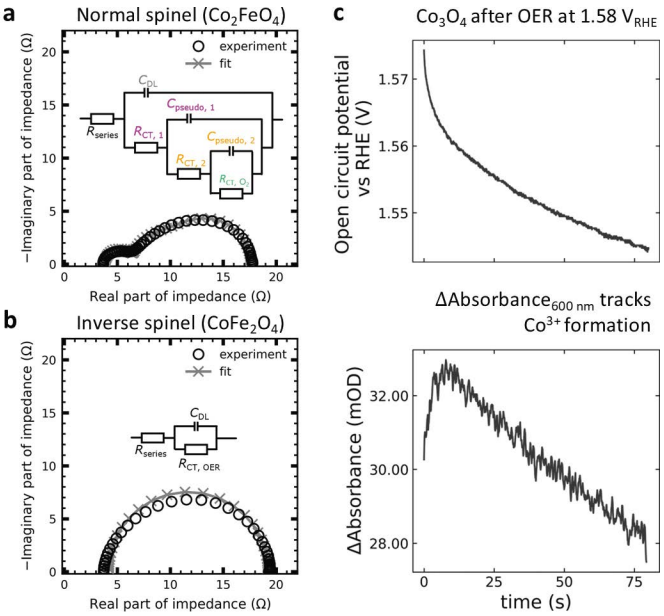

Fig. 2: Pseudocapacitive charge storage allows OER-related processes to be resolved. a, b) Electrochemical impedance spectra recorded during alkaline OER for a) normal spinel Co_2FeO_4 and b) inverse spinel $CoFe_2O_4$ electrodes, including the equivalent circuit models. For the normal spinel, pseudocapacitive contributions allow several OER subprocesses to be distinguished, whereas the inverse spinel response is dominated by one time constant, consistent with OER-related electron transfer occurring in parallel with the double-layer capacitance. c) OCP decay (top) of a Co_3O_4 electrode after polarization in the OER regime and simultaneously recorded absorbance difference at 600 nm (bottom), which is proportional to the amount of formed Co^{3+} sites. The initial increase in absorbance while the OCP decreases indicates self-discharge of higher-valent cobalt cation sites formed during oxygen evolution. Panels a,b adapted from Xiang *et al.* [6, 7] under CC BY 4.0; panel c redrawn based on Kampermann *et al.* [5].

Pseudocapacitive charge storage is therefore not only a complication in electrochemical analysis. It can also make OER-related subprocesses experimentally accessible. This becomes clear in electrochemical impedance spectroscopy (EIS) [6]. For normal spinel Co_2FeO_4, which exhibits pronounced pseudocapacitive behavior, several time constants can be resolved during alkaline OER (Fig. 2a). For inverse spinel $CoFe_2O_4$, in contrast, the response is dominated by one time constant (Fig. 2b), although a multistep OER mechanism is still expected. The difference is not that the inverse spinel performs a chemically simpler reaction. Rather, in the normal spinel, charge storage in redox-active states provides additional capacitive reservoirs, allowing individual electron-transfer subprocesses to appear separately in the impedance spectrum.

This concept can then be applied to Co_3O_4 itself. In *operando* surface X-ray diffraction (SXRD)/EIS experiments on electrodeposited epitaxial Co_3O_4(111), the same type of pseudocapacitive equivalent-circuit description was used to follow charge-transfer resistances before and after thermal annealing (Fig. 3) [7]. Annealing strongly suppresses the pseudocapacitive current and the reversible formation of the amorphous oxyhydroxide-like near-surface region. At the same time, the distribution of OER-related charge-transfer resistances changes. The resistance associated with later oxygen formation/release is reduced for the annealed film at more anodic potentials, whereas the resistance related to the second (more anodic) pseudocapacitive cobalt-site conversion is more pronounced in the early OER range.

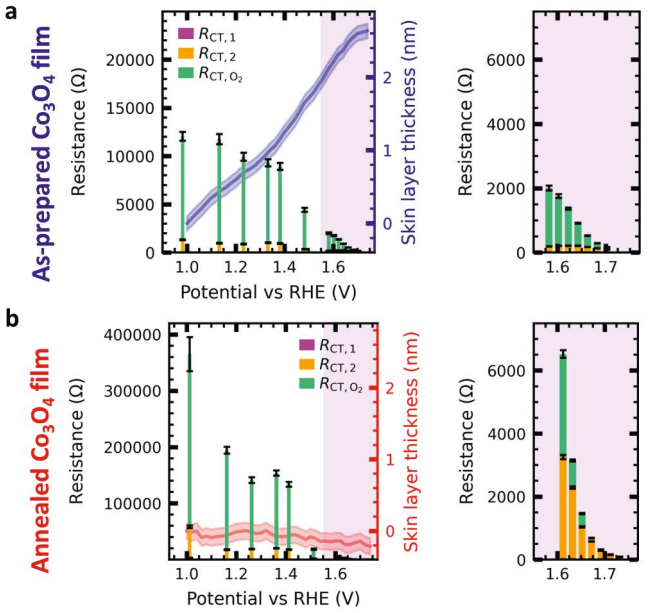

Fig. 3: Potential-induced near-surface transformation and OER subprocesses in Co_3O_4(111). Potential-dependent charge-transfer resistances obtained from *operando* SXRD/EIS measurements of the same epitaxial Co_3O_4(111) film a) before and b) after thermal annealing. The resistances were obtained using the equivalent-circuit model introduced in Fig. 2a. The left panels show the full potential range. The right panels enlarge the OER region. The secondary axes show the average thickness of the transformed near-surface region, commonly referred to as the amorphized oxyhydroxide-like skin layer [8, 9], derived from *operando* SXRD and included as blue and red lines for the as-prepared and annealed film, respectively. Thermal annealing suppresses reversible near-surface restructuring and strongly changes the distribution of OER-related charge-transfer resistances, illustrating how the transformation lability of the oxide surface affects the kinetically relevant subprocesses of oxygen evolution. Adapted from Scharf *et al.* [7], under CC BY 4.0.

This shift in the individual resistances is consistent with the activity trends observed in the same study. The as-prepared film, which undergoes reversible near-surface transformation, shows higher activity at low overpotentials. The annealed film, for which this transformation is largely suppressed, exhibits a lower Tafel slope and becomes more active at higher overpotentials. Thus, the transformed near-surface region can promote OER in one potential range, while a more structurally stable surface can be advantageous in another.

These observations show that the role of Co_3O_4 interfacial transformations cannot be reduced to a simple picture. Pseudocapacitive cobalt site transformations, electrolyte uptake, interfacial softening, and near-surface restructuring are connected, but they are not necessarily equivalent to catalytic turnover. The useful question is therefore not whether the catalyst transforms, but which part of the transformation is reversible, potential-dependent, and kinetically coupled to oxygen evolution. Co_3O_4 is a valuable model system because these coupled processes become experimentally visible. The catalyst stores charge first and this charge storage allows us to follow how the working interface forms, changes, and participates in oxygen evolution.

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Prof. Dr. Julia Linnemann

Julia Linnemann studied chemistry at TU Dresden and first encountered the electrochemical properties of hydrous cobalt oxide films as a student assistant at the Leibniz Institute IFW Dresden about 15 years ago. She later completed her doctoral research at IFW Dresden, electrosynthesizing and electrodepositing colourful cobalt-organic framework and -gel materials. From 2020, she led the junior research group Shape-dependent Electrochemistry at Ruhr University Bochum. In 2025, she moved with her group to Paderborn University, where she is Professor of Electrochemical Technology.

Dr. Christian Leppin

Christian Leppin studied chemistry at Clausthal University of Technology, where he first worked with quartz crystal microbalance (QCM) techniques to investigate interfacial processes. In his doctoral research, he developed a fast QCM technique for resolving rapid gravimetric and viscoelastic changes during electrochemical processes. In 2024, he joined the junior research group Shape-dependent Electrochemistry. Following its relocation to Paderborn University in 2025, he focused on *operando* studies of electrochemical interfaces for energy conversion and storage, combining fast QCM with complementary spectroscopy.

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