Potential spikes at transport bottlenecks cause instability of nominally ionic solid electrolytes in electrochemical cells

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Electrochemical devices including solid oxide fuel cells (SOFC)\textsuperscript{1-4}, solid oxide electrolyzer cells (SOEC)\textsuperscript{4-10} and lithium ion batteries (LIB)\textsuperscript{11-13} with an electrolyte sandwiched between two electrodes can operate under reversible modes. Yet reversing the direction of current often provokes unexpected formation of internal phases unanticipated from the phase diagram. For example, internal oxygen bubbles form at the grain boundaries in the zirconia electrolyte of SOEC\textsuperscript{4,7-10}, thus implicating an oxygen pressure that is impossibly high for the oxygen/hydrogen environments of the adjacent electrodes. Another example is Li metal islands, formed inside the Li$_7$La$_3$Zr$_2$O$_{12}$ electrolyte away from the Li metal electrode in an all-solid-state LIB\textsuperscript{14-16}; similar Na metal islands were found in the Na-beta-alumina solid electrolytes of Na-S batteries\textsuperscript{17-19}. Here we explain these and other phenomena in nominally ionic solid electrolytes and electrodes in
simple thermodynamic terms, attributing the unexpected internal phase formation to a large potential spike that arises from the need to overcome the transport bottlenecks in ion or electron transport. Definite rules dictating the occurrence and absence of such phenomena are provided to help predict and mitigate such phase formation, which leads to microstructural instability, poor efficiency and premature failure.

Our work challenges the consensus that the thermodynamic potentials in electrochemical devices are always bounded by their respective boundary values. For example, for SOFC and SOEC, it is thought “oxygen pressure inside the electrolyte will never become higher than the pressure corresponding to the electrode potential of the oxygen electrode and never lower than corresponding to the electrode potential of the hydrogen electrode, irrespective of which mode or condition for the cell operation.”19 Note that the electrode potentials—the boundary values for the electrolyte—must include electrode polarization, which is the overpotential that arises to overcome the sluggish interfacial reactions.20-22 Such a consensus seems infallible given the directional flow of ions and electrons in these devices. But we have found it untenable at internal transport bottlenecks of either ions or electrons where potential spikes can build up across a thin thickness—analagous to non-equilibrium overpotentials at sluggish electrodes. Just like overpotentials at electrodes that are known to initiate damage, these potential spikes enable the internal formation of unexpected phases; almost invariably, they also lead to stresses, distortion, fracture,
and short-circuit causing deterioration and failure of electrochemical devices.\textsuperscript{4,7-10,14-19}

Transport bottlenecks can exist in both ionic and electronic channel of the device. In yttria-stabilized cubic zirconia, abbreviated as YSZ, grain boundaries are reported to have only 1/100\textsuperscript{th} of the oxygen-ion conductivity of the lattice at \( \sim 800^\circ C \),\textsuperscript{23,24} making them transport bottlenecks in the ionic channel in an otherwise fast ion conductor. Transport bottlenecks in the electronic channel can arise from compositional inhomogeneities, but as will be illustrated below, a bottleneck can also arise from disparate redox conditions on two halves of a mixed ionic and electronic conductor that form a p-n junction in the electronic channel\textsuperscript{25}.

We will first illustrate our ideas using a “good” solid electrolyte like YSZ, then generalize it to solid electrolytes and redox-active electrodes of rechargeable batteries. The main ideas are rested in the redox dependence of conductivity (Fig. 1), and unexpected phase formation due to flux blocking (Fig. 2). As schematically shown in Fig. 1, the conductivity of a good solid electrolyte is dominated by a fast ion, such as \( \text{O}^{2-} \) in YSZ, \( \text{Na}^+ \) in beta-alumina solid electrolyte (BASE) and \( \text{Li}^+ \) in \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) (LLZO), whose concentration, hence conductivity, is insensitive to redox conditions. On the other hand, quite generally the electron’s concentration is elevated by reduction and hole’s by oxidation\textsuperscript{25-28}, as required by defect equilibrium\textsuperscript{20-22,29}, even though their contribution to overall conductivity is still minuscule. In the above, electron and hole may have different mobilities, but this does not alter their dependences on \( \mu_{\text{O}_2} \) or \( \mu_{\text{R}} \) (\( \text{R}=\text{Li} \) or \( \text{Na} \)) in Fig. 1. This is because the dependence, again quite generally, originates from the local equilibrium of electronic and lattice...
defects. Such equilibrium is particularly simple in fast ion conductors because their concentration of the dominant lattice defect is fixed by heavy doping. Indeed, it is known that this leads to the same $\mu_{O_2}$ dependence as in Fig. 1 for the electronic conductivities of many $O^{2-}$ electrolytes, including YSZ (Fig. 1), Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$ and La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$.

In the above, local equilibrium in the context of irreversible thermodynamics was mentioned as it is a standard assumption in electrochemistry. But as demonstrated in Supplementary Note 1 it is also fully justified for the nominally ionic solid electrolytes considered in this work under the normal operational conditions of electrochemical cells. In this context, internal potential spikes explored in this work has a different origin from electrode overpotentials: the former is still under local equilibrium, the latter is away from equilibrium. For oxygen, the most important local equilibrium stems from the following reaction

$$O^{2-} = \frac{1}{2}O_2 + 2e^- \quad (1)$$

which demands the electrochemical potential $\tilde{\mu}_i$ of the species $i$, with a charge $z_ie$, to obey the equilibrium condition

$$\tilde{\mu}_{O^{2-}} = \frac{1}{2}\mu_{O_2} + 2\tilde{\mu}_e \quad (2)$$

Here, because $\tilde{\mu}_i = \mu_i + z_i e\phi$, where $\mu_i$ is the chemical potential of the species $i$ and $\phi$ is the electrostatic potential, $\mu_{O_2}$ is used in lieu of $\tilde{\mu}_{O_2}$ for uncharged $O_2$. Likewise, for alkali metal $R$, $R=$Li or Na, local equilibrium

$$R = R^+ + e \quad (3)$$

demands
\[ \mu_R = \bar{\mu}_{R^+} + \bar{\mu}_e \]  
(4)

Note that a reducing condition is met at high Li activities or low \( \text{O}_2 \) activities, and an oxidizing condition at low Li activities or high \( \text{O}_2 \) activities.

![Conductivities in solid electrolyte](image)

**Figure 1 Conductivities in solid electrolyte.** Conductivities vs. \( \mu_{\text{O}_2} \) in YSZ (800 \( ^\circ \)C) showing redox-insensitive ionic conductivity overwhelming redox-dependent electronic conductivities\(^{25}\). Similar trends also expected for conductivities in fast-\( R^+ \) solid electrolyte (\( R=\text{Li, Na} \)) vs. \( \mu_{R} \)\(^{26-28}\). A solid electrolyte with two boundary \( \mu_{\text{O}_2} \) values located on two sides of the \( \sigma_e-\sigma_h \) intersect has a p-n junction in the electronic channel—one half having mostly electron conduction and the other half hole conduction—even though the ionic channel always dominates.
Figure 2: Exemplary unexpected phase formation caused by transport bottlenecks. Left: oxygen gas bubbles and reduction voids due to blocking of oxygen ions; right: sodium metal islands due to blocking of sodium ions. In both cases, unexpected phases preferentially form on transverse grain boundaries because they block the ion flow the most, which causes potential overshoot and undershoot, providing thermodynamic driving force for phase formation.

We now consider a transport bottleneck somewhere in the ionic or electronic channel. We let it extend over a thickness $t$ in the current direction, with $t \ll L$, the electrolyte length. Here, cracks are not considered since they do not allow any flow. At the steady state, because the flow in both channels must remain constant, a blockage in either channel will force a discontinuous $\mu_{O_2}$ across $t$ in the $t \to 0$ limit in the following ways. (i) At an ionic bottleneck that is not an electronic bottleneck, to maintain the constant ion flow there must be a discontinuous change of $\bar{\mu}_{O_2}$ across $t$. But $\bar{\mu}_e$ is continuous, hence $\delta \bar{\mu}_e = 0$ in the $t \to 0$ limit. This implies $\delta \mu_{O_2} \neq 0$ according to Eq. (2). (ii) At an electronic bottleneck that is not an ionic bottleneck, to maintain the constant electron flow there must be a discontinuous change of $\bar{\mu}_e$
across $t$. But $\tilde{\mu}_{O^2^-}$ is continuous, hence $\delta\tilde{\mu}_{O^2^-} = 0$ in the $t\to0$ limit. This again implies $\delta\mu_{O_2} \neq 0$ according to Eq. (2).

We next determine the signs of potential discontinuities across $t$ from the directions of ion and electron flows. (See Methods on how they are assigned.) First consider the ion flow with a bottleneck. In a SOFC, $O^{2-}$ flows to the left in Fig. 3a from the oxygen electrode to the hydrogen electrode. So the abrupt drops in $\tilde{\mu}_{O^2^-}$ and $\mu_{O_2}$ across $t$ are both from right to left, and the overall $\mu_{O_2}$ profile taking into account the drop and the boundary condition is always bounded by the boundary values (Fig. 3e, upper panel). In contrast, in a SOEC, $O^{2-}$ flows to the right from the hydrogen electrode to the oxygen electrode in Fig. 3b, so the abrupt drops in $\tilde{\mu}_{O^2^-}$ and $\mu_{O_2}$ across $t$ are both from left to right (Fig. 3f, upper panel). This allows the overall $\mu_{O_2}$ profile to exceed the bounds specified by the boundary potentials—to be referred to as a potential overshoot/undershoot—if $\delta\tilde{\mu}_{O^2^-} = \delta\mu_{O_2} / 2$ is large enough, which is realized when the blockage is severe enough and the $O^{2-}$ flow is large enough. Note that a non-monotonic $\mu_{O_2}$ profile does not contradict any physics because $\tilde{\mu}_{O^2^-}$ and $\bar{\mu}_e$ can still be monotonic due to the $z_e e \phi$ contribution. Besides, there should be no $O_2$ gas transport in the solid electrolyte anyway.
Figure 3 Potential overshoot/undershoot in solid electrolyte. Schematics of solid electrolyte in (a) SOFC and (b) SOEC showing directions of ionic flow $J_{O^2^-}$ and electron flow $J_e$ (hole flow in the opposite direction). Also shown are schematic profiles of discontinuous $\mu_{O_2}$ across a bottleneck in either the ionic channel (upper panel of (e-f)) or the electronic channel (lower panel of (e-f)). Analogous schematics of solid electrolyte also shown for LIB and Na-S battery in (c) discharge and (d) charge. Since ionic conduction dominates in a good electrolyte, the total current flow is determined by the ion flow. Note $O_2$ and $R$ are the respective underlying molecular/atomic species of the fast ions ($O^{2-}$ and $R^+$) in the solid electrolyte. Note...
that these are nominally ionic solid electrolytes in which $J_e$ is minuscule, but for clarity the lengths of the $J_e$ arrows are grossly overexaggerated in the schematics.

The same reasoning applied to the electron flow does not lead to any $\mu_{O_2}$ overshoot/undershoot. Electrons flow to the right in both SOFC and SOEC in Fig. 3a-b, so the abrupt drop in $\bar{\mu}_e$ is always from left to right. According to Eq. (2), this causes an opposite drop in $\mu_{O_2}$, from right to left, and $\mu_{O_2}$ is always bounded by the boundary potentials (Fig. 3e-f, lower panel). Therefore, the only internal location where an unexpected oxygen phase (e.g., oxygen bubble and reduction-induced void) may form is from a $\mu_{O_2}$ overshoot/undershoot developed at an ionic bottleneck in SOEC.

Very similar outcomes are depicted in Fig. 3c-d for a fast, nominally ionic solid electrolyte in a rechargeable battery. Examples of solid electrolytes are BASE in the Na-S battery and LLZO in a LIB paired with a Li metal anode. On the right is an $R$ metal electrode with a $\mu_R$ that takes the value of metal’s chemical potential, which is the highest and the most reducing value possible for the device. On the left is a positive electrode, e.g., a sulfur electrode in a Na-S battery or LiFePO$_4$ in LIB, with a lower $\mu_R$. During charging, $R^+$ flows through the electrolyte from left to right returning $R^+$ to the $R$ electrode, and electrons flow through the electrolyte from right to left. (See Methods on how the flow directions are determined.) As shown in Fig. 3f, a transport bottleneck in the ionic channel can elevate $\mu_R$ to levels above the value of $R$ metal, but a bottleneck in the electronic channel cannot. During discharging, as
the \( R \) electrode dispenses \( R^+ \), both \( R^+ \) and electrons flow through the electrolyte to the left as shown in Fig. 3c; here \( \mu_e \) is always bounded by the boundary values (Fig. 3e).

Thus, the only internal location where an unexpected \( R \) phase (e.g., \( R \) metal islands away from the electrode) may form is at an ionic bottleneck during charging. Comparing batteries with solid oxide cells, we can see that battery charging is analogous to SOEC, and it is in these modes that an unexpected phase may form at an internal location of ionic bottleneck inside solid electrolyte where a potential overshoot/undershoot develops at high enough current densities. (The analogy is exact if we use hole—the antiparticle of electron—instead of electron in the oxygen cells in Fig. 3.)

Because YSZ has the most comprehensive conductivity data available over a wide range of redox conditions\(^{25} \), we have calculated all the potentials for YSZ to quantitatively assess the kinetically driven overshoots/undershoots envisaged above. (See Methods for formulation of the calculation.) In the upper panels of Fig. 4a-b, \( \mu_{O_2} \) profiles in a YSZ SOEC at 800 °C are shown for a polycrystalline electrolyte with \( L=10 \mu m \). Bounded by a hydrogen electrode at \( x=0 \) and an oxygen electrode at \( x=L \), it has three grain boundaries at \( x=\frac{1}{4}L, \frac{1}{2}L \) and \( \frac{3}{4}L \), the last (in Fig. 4a) or first (in Fig. 4b) one allowed an \( O^{2-} \) conductivity ratio \( \sigma_{O^2-}^{\text{GB}} / \sigma_{O^2-}^{\text{L}} \) set as \( 10^{-2}, 10^{-3}, \) or \( 10^{-4} \), while \( \sigma_{O^2-}^{\text{GB}} = \sigma_{O^2-}^{\text{L}} / 100 \) for everyone else. (See middle panels of Fig. 4a-b.) Under similar operating conditions (boundary oxygen potentials and current density) used by Ref. 4, the \( \mu_{O_2} \) drops in Fig. 4 (upper panels) at grain boundaries are all from left to right, with the most pronounced drop at the boundary that experiences the most severe
ionic blockage. With \( \frac{\sigma_{O^2-}^{\text{cm}}}{\sigma_{O^2-}^{\text{lin}}} = 10^{-4} \), \( \mu_{O_2} \) at the last grain boundary in Fig. 4a exceeds the boundary potential at \( x=L \), whereas \( \mu_{O_2} \) at the first grain boundary in Fig. 4b falls below the boundary potential at \( x=0 \). So the overshoot/undershoot schematics in Fig. 3f for SOEC with an ionic bottleneck are confirmed. For SOFC, similar calculations shown in Fig. S1 in Supplementary Information found drops of an opposite direction and no \( \mu_{O_2} \) overshoot/undershoot at any grain boundary in agreement with Fig. 3e. As expected, despite the discontinuities in \( \mu_{O_2} \), \( \tilde{\mu}_{O^2-} \) and \( \tilde{\mu}_e \) (in the lower panels of Fig. 4a-b and parallel plots in Fig. S1) are monotonic in a way consistent with the flow directions of \( O^{2-} \) and electrons. Lastly, the strong redox dependence shown in Fig. 1 for electron and hole conductivities is manifest in the middle panels of Fig. 4 and Fig. S1: hole conductivity increases with increasing \( \mu_{O_2} \), electron conductivity increases with decreasing \( \mu_{O_2} \), and the two halves form a p-n junction. Importantly, at the very junction where the combined electronic conductivity, \( \sigma_e + \sigma_h \), has a sharp minimum, there is a sharp rise in \( \mu_{O_2} \) from left to right in all the calculations. This is too predicted by Fig. 3: an electronic bottleneck—here the p-n junction that naturally arises from the redox boundary condition—causes \( \mu_{O_2} \) to jump from left to right but remain bounded by the boundary values. In short, every detail predicted by Fig. 3 is confirmed by these calculations. Moreover, they affirm that, notwithstanding its minuscule magnitude evidenced by the very small electronic transference numbers (from 0.0014 to 0.0029) of the polarized devices cited in the caption of Fig. 4, the redox-sensitive electronic conductivity in a nominally ionic solid electrolyte is decisively important for determining the redox profile and the
existence of a p-n junction serving as an electronic bottleneck.\textsuperscript{20-22,29}

Figure 4 Calculated potentials and conductivities in SOEC. Polycrystalline YSZ electrolyte in SOEC at $\SI{-1}{A/cm^2}$ with grain boundaries at $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$ from left and (a) $\sigma_{O^2^-}^{\text{Last GB}}/\sigma_{O^2^-}^{\text{L}}$ and (b) $\sigma_{O^2^-}^{\text{First GB}}/\sigma_{O^2^-}^{\text{L}}$ set as $10^{-2}$, $10^{-3}$, or $10^{-4}$, while all other boundaries set at $10^{-2}$. Upper panels: $\mu_{O_2}$ with dashed lines indicating boundary $\mu_{O_2}$ at two electrodes. Insets show apparently unbounded overshoot is mathematically possible. Middle panels: conductivities of $O^2^-$, electrons and holes, for $\sigma_{O^2^-}^{\text{Last/first GB}}/\sigma_{O^2^-}^{\text{L}} = 10^{-4}$. Lower panels: electrostatic potential $\phi$, electrochemical
potentials and chemical potentials of $O^{2-}$ and e, for $\sigma_{O^{2-}\text{GB}}^{\text{L}} / \sigma_{O^{2-}}^{L} = 10^{-4}$. Other conditions: 800 °C with $\mu_{O_2}^f = -5.11 \text{ eV (PO}_2=10^{-24} \text{ atm)}$ at $x=0$, $\mu_{O_2}^r = 0.21 \text{ eV (PO}_2=10 \text{ atm)}$ at $x=L$, $L=10 \mu\text{m}$, $t=10 \text{ nm}$. Calculated ionic vs. electronic transference numbers for these polarized devices are 0.9986 vs. 0.0014 for black curve in (a), 0.9985 vs. 0.0015 for red curve in (a), 0.9978 vs. 0.0022 for blue curve in (a), 0.9986 vs. 0.0014 for black curve in (b), 0.9984 vs. 0.0016 for red curve in (b), and 0.9971 vs. 0.0029 for blue curve in (b).

We have repeated the calculations for another set of SOEC with a hypothetical solid electrolyte of the same ionic conductivity but whose electron and hole conductivities, though still quite weak, are 100 times those of YSZ at all $\mu_{O_2}$ (Fig. S2a). Very similar potential overshoot/undershoot is again found at the blocking grain boundary (Fig. S2b-c), but the new devices have a calculated electronic transference number of 0.39 (Fig. S2b) and 0.46 (Fig. S2c), meaning it has become nominally mixed conducting because of polarization. Indeed, the stronger electronic conduction leaves a weaker ionic conduction at the device level, which gives rise to a weaker overshoot/undershoot in Fig. S2b-c. These results are possibly applicable to devices where YSZ is replaced by Gd-doped ceria (GDC), which is still nominally ionic but has more notable electronic conduction.30

Unlike electrons and holes that are strongly redox sensitive, the concentration of the fast ionic species should be fixed in a good solid electrolyte operating within the electrolytic regime. Such is the case for YSZ, in which $\mu_{O^{2-}}$ is fixed throughout the
electrolyte via heavy Y\textsuperscript{3+} doping. This affords further details to be extracted from Eq. (2), rewritten below in \( \mu \),

\[
\mu_{O^2^-} = \frac{1}{2} \mu_{O_2} + \mu_e
\]  

(5)

Given

\[
\tilde{\mu}_{O^2^-} = \mu_{O^2^-} - 2e\phi
\]  

(6)

and a constant \( \mu_{O^2^-} \), any \( \delta\mu_{O_2} \) must be accompanied by a \( \delta\mu_e = -\frac{1}{2}\delta\mu_{O_2} \) (hence the large redox sensitivity of electron and hole concentrations), and any \( \delta\tilde{\mu}_{O^2^-} \) must be accompanied by \( e\delta\phi = -\frac{1}{2}\delta\tilde{\mu}_{O^2^-} \). These predictions are verified in the lower panels of Fig. 4 and Fig. S1. Clearly, a highly non-linear \( \tilde{\mu}_e \) is needed to maintain a constant electronic flow in the face of a hugely varying \( \sigma_e + \sigma_h \)—it is such a strong nonlinearity that makes numerical calculations necessary in constructing Fig. 4 and Fig. S1. In contrast, a constant oxygen ion conductivity allows \( \tilde{\mu}_{O^2^-} \) to follow a straight line except at \( O^2^- \)-blocking grain boundaries where the flow continuity is maintained by \( e\delta\phi = -\frac{1}{2}\delta\tilde{\mu}_{O^2^-} \). Therefore, some voltage must be spent at each ionic bottleneck, resulting in an increase in the overall electrolyte resistance. (There is no voltage drop at electronic bottlenecks because \( \delta\tilde{\mu}_{O^2^-} = 0 \).

Although the calculations were performed for YSZ electrolytes, in view of Fig. 1 we expect the main conclusions drawn from them are also applicable to fast \( R^+ \) electrolytes of weak electronic conduction in rechargeable batteries. Below we will compare them with the experimental observations in these electrolytes, summarized in Table S1 in Supplementary Information.

First, there are the long-standing findings of oxygen bubbles at YSZ grain
boundaries in SOEC near the oxygen electrode, especially at high current densities and during long operation.\textsuperscript{4,7-10} They were attributed to oxygen overpotential at the oxygen electrode, which elevates the oxygen potential in the nearby YSZ electrolyte.\textsuperscript{4,7,8,20-22} However, such a mechanism should have caused bubble formation at all grain boundaries near the oxygen electrode and especially at their triple/quadruple-grain junctions, because they all see the same driving force and they are all favorable nucleation sites. Yet most bubbles and their coalescence cracks were found on transverse grain boundaries, displaying a propensity for longer boundaries and no preference for triple/quadruple junctions. This can be understood by our model because the $\text{O}_2^-$ flow on the longitudinal boundaries is easily diverted to the grain interior nearby, but diversion is too difficult for longer, transverse boundaries, so they constitute very effective ionic bottlenecks. Moreover, as bubbles accumulate, the area of the intact grain boundary decreases, so it must support a higher local current density to sustain the constant ion flow, which in turn necessitates a larger voltage drop and an overall resistance increase. Therefore, not only our mechanism foresees an internal potential overshoot at transverse boundaries, it also anticipates the experimentally observed accelerated SOEC degradation. On the other hand, SOFC is known not to suffer from the same problem, in agreement with our prediction. Indeed, in Ref. 4 whose test parameters were used in calculating Fig. 4 and Fig. S1, it was discovered that alternating the current direction and operating between the SOEC and SOFC modes can suppress bubble formation. This is understandable by comparing Fig. 4a (for SOEC) and Fig. S1a (for SOFC), because the SOFC operation will very
effectively eliminate the internal potential spikes. Lastly, the $\mu_{O_2}$ undershoot below the left-electrode $\mu_{O_2}$ in the SOEC mode (Fig. 4b) also finds support in our recent YSZ study: under severe reduction, oxygen-vacancy cavities (and their coalescence cracks) preferentially form along the transverse grain boundaries near the hydrogen electrode$^{33,34}$. Note that electrons are needed for maintaining charge neutrality at (i) oxygen bubbles, where $O^{2-}$ precipitation must be accompanied by electron out-diffusion, and (ii) vacancy cavities, where $V_{O}^{\bullet\bullet}$ precipitation must be accompanied by electron in-diffusion. Indeed, under normal operational conditions, 

**Supplementary Note 2** shows that the minuscule electronic conductivity in YSZ (and LLZO below) can supply the necessary electronic current across the nominally ionic solid electrolyte for the formation of neutral phases without causing an increase in the apparent device resistance. Therefore, electrons are an integral part in damage accumulation that involves the internal formation of unexpected phases.$^{20-22,29}$

For rechargeable batteries, BASE and LLZO with weak electronic conduction and fast ionic conduction are known as good solid electrolytes for Na-S batteries and LIB, respectively. In 1970-1980s, failure-causing internal Na metal deposits were observed during Na-charging ($\mu_{Na}$ overshoot in Fig. 3, in analogy to $\mu_{O_2}$ overshoot in Fig. 4a) in BASE.$^{17-19}$ While they were often found at cracks and voids thus motivated the explanation based on electrical-field/current concentrations, they also formed at triple-grain junctions and two-grain boundaries—again primarily transverse ones that blocked the Na$^+$ flow. Since Na$^+$ in BASE moves inside the open “galleries” between spinel blocks$^{34}$, Na$^+$ conduction is highly anisotropic and much slower in
some grains and across most grain boundaries\textsuperscript{36,37}. Therefore, ionic bottlenecks can explain the deposits at cracks, voids and transverse grain boundaries. Interestingly, next to the sulfur electrode, BASE dissolution causing graphite (serving as a charge connector for the sulfur electrode) imprint was also observed.\textsuperscript{35} This indicates that the $\mu_{\text{Na}}$ of BASE is so low there that it becomes unstable, causing dissolution, and such undershoot is too predicted by Fig. 3f under ionic blockage. Rather similar observations of failure-causing internal Li metal deposits were recently reported for LLZO\textsuperscript{14-16}, with the analogy to Na metal deposits in BASE duly noted. The deposit sites again include grain boundaries suggesting ionic bottlenecks. Finally, relatively uniform precipitation of Na metal without preference to the transverse grain boundaries was also seen in BASE in a zone next to the Na electrode, and such zone propagates inward with time.\textsuperscript{35} (The analogy in LLZO has again been reported very recently.\textsuperscript{16}) This may be explained by the $\sigma_e + \sigma_h$ minimum, i.e., the p-n junction, which as an electronic bottleneck can cause $\mu_{\text{Na}}$ to become very close to the boundary $\mu_{\text{Na}}$. This could trigger the general precipitation of a Na-rich alloy, at locations that are not limited to flow-blocking planar defects. Subsequent short circuiting across the zone may develop as precipitates grow, which will move the $\mu_{\text{Na}}$ profile inward and induce more precipitation.

We believe our mechanism can also explain metal deposits in solid electrolyte interphase (SEI) that forms between the negative electrode and electrolyte, and instability of cathode electrolyte interphase (CEI) that forms between the positive electrode and electrolyte. If they are at all beneficial in LIB, these interphases must be
fast ion conductors and nearly electron insulators. So they may again be regarded as good electrolyte despite their very thin thickness. Quite often, SEI and CEI are chemically and microstructurally heterogeneous, so it is likely that they contain some ionic/electronic bottlenecks. Applying Fig. 3 (with more details shown in Fig. S3) to SEI/CEI, we expect $\mu_R$ overshoots/undershoots at ionic bottlenecks during charging. In support of this, on the more reduced side (i.e., SEI), internal Li metal deposits at 20-30 nm from the surface were found in the SEI on the graphite anode after cycling, indicating the internal $\mu_{Li}$ there had reached the level of Li metal and exceeded SEI’s upper boundary $\mu_{Li}$. This will compromise the integrity of SEI as a very thin membrane of selective transport. Indeed, in the original paper that proposed the SEI concept, internal Li metal precipitation speculated to arise from excessive local heating was suggested as a cause for unstable SEI. The situation at CEI could be worse, for being on the more oxidized side, highly destructive O$_2$/CO$_2$ bubbles would form inside upon any severe internal $\mu_{Li}$ undershoot.

Interestingly, unexpected Li metal precipitation has also been observed in LIB anodes when they are cycled above 0 V vs. Li/Li$^+$, suggesting a $\mu_{Li}$ overshoot. For example, Li metal precipitation occurred inside a porous graphene network on the negative electrode side, tested against a Li metal electrode in the half-cell configuration between 3.0 V and 0.03 V. Conversely, the frequent report of O$_2$/CO$_2$ evolution from the positive electrodes may be taken as tentative evidence of $\mu_{Li}$ undershoots on the more oxidized side. Good redox-active advanced electrodes should have facile electronic conductivity, and many of them also enjoy a broad range
of stoichiometry and valence states for transition-metal cations or even anions. Therefore, as a first approximation for the electrode, it seems reasonable to assume a constant $\bar{\mu}_e$ instead of a constant $\mu_{Li^+}$ as before. This implies any gradient in $\bar{\mu}_{Li^+}$ will be reflected in a gradient of $\mu_{Li^+}$. Since Li$^+$ diffusion in the electrode is likely to be slower than that in the electrolyte, one may expect a graded $\bar{\mu}_{Li^+}$ to develop in the electrode, which suffices to specify its $\mu_{Li^+}$ as shown in Fig. 5 (i.e., the Li$^+$ rate-limiting case). This knowledge allows us to predict their $\mu_{Li^+}$ overshoot/undershoot at an electronic bottleneck. On the other hand, some redox-active electrodes in use, e.g., LiFePO$_4$, do suffer from relatively poor electronic conductivity and need a conductive coating, so the other extreme of the approximation for the electrode is to assume a constant $\bar{\mu}_{Li^+}$. This implies any gradient in $\bar{\mu}_e$ will be reflected in a gradient of $\mu_{Li^+}$, and as shown in Fig. 5, their overshoot/undershoot now occurs at an ionic bottleneck.

Further considering the highly oxidizing condition (low $\mu_{Li^+}$) on the positive electrode side especially at high voltages and vice versa on the negative electrode side at low voltages, we believe the most significant scenarios are a $\mu_{Li^+}$ undershoot in the former, and a $\mu_{Li^+}$ overshoot in the latter. For the positive electrode, a $\mu_{Li^+}$ undershoot and O$_2$/CO$_2$ formation is likely to happen (i) at an ionic bottleneck in the electron rate-limiting case, or (ii) at an electronic bottleneck in the Li$^+$ rate-limiting case during delithiation (i.e. charging) at high voltages. For the negative electrode, a $\mu_{Li^+}$ overshoot and Li metal formation is likely (iii) at an ionic bottleneck in the electron rate-limiting case, or (iv) at an electronic bottleneck in the Li$^+$ rate-limiting
case during lithiation (i.e. charging) at low voltages. Therefore, our theory (iii or iv) can explain why Li metal precipitates in Ref. 40. To definitively correlate O$_2$/CO$_2$ evolution$^{41,42}$ to our theory (i or ii), we recommend the following experiment: in a half-cell configuration and with the same cut-off voltage, observe faster O$_2$/CO$_2$ gas generation starting at a lower voltage when the cell delithiates at a faster charge rate.

| Electrodes of LIB | Equilibrium: $\mu_{Li} = \tilde{\mu}_{Li^{+}} + \tilde{\mu}_e$ |
|-------------------|---------------------------------------------------------------|
| Lithiation         | (a) Electrolyte | $J_{Li^{+}}$ | $J_e$ | Current collector |
| Delithiation      | (b) Electrolyte | $J_{Li^{+}}$ | $J_e$ | Current collector |

| Li$^+$ rate-limiting |
|----------------------|
| Ion blocked           |
| Electron blocked      |
| Overshoot             |
| Undershoot            |

| Electron rate-limiting |
|------------------------|
| Ion blocked            |
| Electron blocked       |
| Overshoot              |
| Undershoot             |

Figure 5 Potential overshoot/undershoot in active electrodes. Schematics of (a) lithiation and (b) delithiation of electrodes for LIB showing directions of ionic flow $J_{Li^{+}}$ and electron flow $J_e$ (hole flow in the opposite direction). Two extreme cases
considered: (c-d) Li$^+$ rate-limiting with constant $\bar{\mu}_c$, and (e-f) electron rate-limiting with constant $\bar{\mu}_e$. Also shown are schematic profiles of $\mu_{Li}$ with a jump across a bottleneck in the ionic channel (upper panel of (c-f)) or in the electronic channel (lower panel of (c-f)). Note that the lengths of $J_{Li}$ and $J_e$ arrows are not accurate and meant for schematics only.

Our theory identifies transport bottlenecks as the root cause for unexpected phase formation that may result in accelerated degradation. Sample calculations in Fig. S4 for YSZ electrolyte demonstrate that an increasing number of severely ion-blocking grain boundaries increases the total voltage across the SOEC, which means an increase in the total internal resistance of SOEC as has been often reported. Our theory is consistent with the common knowledge that high current densities are more damaging to electrochemical devices, and low temperature operations such as running a battery in a frigid weather makes the matter worse. Conversely, just like alternating between SOEC and SOFC operation can prolong the device lifetime$^4$, resting at a lower (or zero) current without changing the mode will help by substantially removing the $\mu_{O_2}$ overshoot. Similar resting at a smaller charge rate or pulse charging may also help batteries. To avoid bottlenecks, coarse microstructural inhomogeneities (e.g., coating, connectors, pores, wetting) should be minimized. Naturally, nano-sized grains will help divert the flow around blocking grain boundaries, but columnar grains aligned in the flow direction may too diseffectuate most flow-blocking transverse boundaries. Our theory further makes a few new
observations, some of which go against the conventional wisdom. On the ionic side, dopants that lower the space charge should make grain boundaries less ion blocking\textsuperscript{23,24}, and reducing diffusion anisotropy in the lattice will likely obviate ionic bottlenecks. So along this line the theory suggests glass and liquid are preferred over polycrystalline solid electrolyte, notwithstanding the fact that dendrite may still form in liquid electrolyte for an altogether different reason. On the electronic side, although the conventional wisdom is to minimize electronic conductivity, our model calculations in Fig. S5 actually finds donor or acceptor dopants providing just a small amount of redox-insensitive electron or hole conductivity can already greatly smooth out the p-n junction and lessened its effect as an electronic bottleneck, thus ameliorating the sharp redox potential profiles and reducing the chance of potential overshoots/undershoots. Even at an ionic bottleneck such as a grain boundary, according to Eq. (A11) the potential overshoot can be entirely eliminated if the ratio of electronic conductivity to ionic conductivity at the grain boundary is kept the same as that in the lattice. Therefore, increasing the lattice electronic conductivity will help as much as lowering the grain boundary electron conductivity or increasing the grain boundary ionic conductivity. These findings have exemplified the power of thermodynamics in a general analysis when the assumption of local equilibrium is justified. Future analysis possibly aided by first-principles calculations\textsuperscript{43} and model experiments to advance our understanding of unexpected phase formation in electro-active devices can help improve their reliability further.
Methods

Directions of ion and electron flows

Consider the YSZ electrolyte in Fig. 3a-b and write the potential differences between the oxygen electrode and the hydrogen electrode as \( \Delta \mu_{O_2}, \Delta \mu_{O^{2-}}, \Delta \mu_e \), and \( \Delta \phi \).

They satisfy the equilibrium condition \( \Delta \mu_{O^{2-}} = \frac{1}{2} \Delta \mu_{O_2} + 2 \Delta \mu_e \). For YSZ whose oxygen concentration is controlled by Y, \( \Delta \mu_{O^{2-}} = 0 \), thus \( \Delta \mu_e = -\frac{1}{4} \Delta \mu_{O_2} \). Therefore, given the boundary condition \( \Delta \mu_{O_2} > 0 \), the only free variable left is \( \Delta \phi \) that determines the modes of operation and directions of flows: the direction of \( O^{2-} \) flow by \( \Delta \tilde{\mu}_{O^{2-}} = -2e\Delta \phi \), and that of electron flow by \( \Delta \tilde{\mu}_e = \Delta \mu_e - e\Delta \phi = -\frac{1}{4} \Delta \mu_{O_2} - e\Delta \phi \).

When \( \Delta \phi > 0 \), \( O^{2-} \) flows from the hydrogen electrode to the oxygen electrode, which is the case of SOEC. Conversely, when \( \Delta \phi < 0 \), \( O^{2-} \) flows from the oxygen electrode to the hydrogen electrode, which is the case of SOFC. For electrons, throughout the SOEC range, \( \Delta \phi > 0 \), so electrons flow from the hydrogen electrode to the oxygen electrode; in the SOFC range up to \( -\frac{1}{4} \Delta \mu_{O_2}/e < \Delta \phi < 0 \), electrons also flow from the hydrogen electrode to the oxygen electrode. When \( \Delta \phi = -\frac{1}{4} \Delta \mu_{O_2}/e < 0 \) is reached, it corresponds to short-circuiting the external circuit, thus the range beyond which is of no practical interest. This explains all the directions of \( O^{2-} \) ion and electron flows in Fig. 3a-b.

The same argument applies to solid electrolytes for \( Li^+ \) and \( Na^+ \), where we have \( \Delta \mu_{Li^+/Na^+} = 0 \). Therefore, \( \Delta \tilde{\mu}_{Li^+/Na^+} = e\Delta \phi \), \( \Delta \mu_e = \Delta \mu_{Li/Na} \), and \( \Delta \tilde{\mu}_e = \Delta \mu_{Li/Na} - e\Delta \phi \).

During charging, \( \Delta \phi < 0 < \Delta \mu_{Li/Na}/e \), so ion flows to the right (i.e., Li/Na metal electrode) and electrons to the left (i.e., cathode). During discharging,
$0 < \Delta \phi < \Delta \mu_{\text{Li/Na}} / e$, so both ions and electrons flow to the left (i.e., cathode) from the Li/Na metal electrode. When $\Delta \phi = \Delta \mu_{\text{Li/Na}} / e > 0$ is reached, it corresponds to short-circuiting the external circuit thus the range beyond which is of no practical interest. This explains all the directions of ion and electron flows in Fig. 3c-d for Li$^+$ and Na$^+$ electrolytes.

**Solving $\mu_{O_2}$ and other potentials in YSZ electrolyte**

With $\mu'_{O_2} < \mu''_{O_2}$ at the two boundaries $x=0$ and $x=L$ (where $L$ is the thickness of the electrolyte) in Fig. 4, we will solve the steady-state distributions of potentials in the YSZ slab under a prescribed total electrical current density $j_{\text{total}}$, defined as positive if it flows from the left to the right. We adopt the more general method previously developed by us$^{29}$, but simplify it by excluding internal reactions. The notation below is the same as in Ref. 29. We consider four species: oxygen ion $O^{2-}$, oxygen molecule $O_2$, electron $e$ and hole $h$. Under local equilibrium, the two chemical reactions

$$O^{2-} = \frac{1}{2}O_2 + 2e \quad (A1)$$
$$e + h = \text{nil} \quad (A2)$$

relate the three electrochemical potentials and the chemical potential $\mu_{O_2}$ of $O_2$ by

$$\tilde{\mu}_{O^{2-}} = \frac{1}{2} \mu_{O_2} + 2 \tilde{\mu}_e \quad (A3)$$
$$\tilde{\mu}_e + \tilde{\mu}_h = 0 \quad (A4)$$

We assume no mobile $O_2$ molecule in the solid electrolyte. The only fluxes are that of charged species
\[ j_{o^-} = \frac{\sigma_{o^-} \, d\tilde{\mu}_{o^-}}{2e \, dx} \]  \hspace{1cm} \text{(A5)}

\[ j_{e} = \frac{\sigma_{e} \, d\tilde{\mu}_{e}}{e \, dx} \]  \hspace{1cm} \text{(A6)}

\[ j_{h} = -\frac{\sigma_{h} \, d\tilde{\mu}_{h}}{e \, dx} = \frac{\sigma_{h} \, d\tilde{\mu}_{e}}{e \, dx} \]  \hspace{1cm} \text{(A7)}

where \( \sigma_{i} \) denotes the conductivity of species \( i \), which varies as a function of local \( \mu_{o_{i}} \) and structure, i.e., being in the lattice or at a grain boundary. Since electrons and holes can be generated and annihilated via Eq. (A2) and they follow Eq. (A4, A6-7), we combine their current densities to a total electronic current density \( j_{eh} \)

\[ j_{eh} = j_{e} + j_{h} = \frac{\sigma_{e} + \sigma_{h} \, d\tilde{\mu}_{e}}{e \, dx} \]  \hspace{1cm} \text{(A8)}

At the steady state and without crosstalk between ionic and electronic currents (because we assumed no internal reactions, unlike Ref. 29), the ionic current density \( j_{o^-} \) and the electronic current density \( j_{eh} \) must each remain constant throughout the electrolyte. Therefore, derivatives of \( \tilde{\mu}_{i} \) can be expressed in terms of \( j_{o^-} \) and \( j_{eh} \) via Eq. (A5) and (A8),

\[ \frac{d\tilde{\mu}_{o^-}}{dx} = 2e \frac{j_{o^-}}{\sigma_{o^-}} \]  \hspace{1cm} \text{(A9)}

\[ \frac{d\tilde{\mu}_{e}}{dx} = -\frac{d\tilde{\mu}_{h}}{dx} = e \frac{j_{eh}}{\sigma_{e} + \sigma_{h}} \]  \hspace{1cm} \text{(A10)}

Using Eq. (A9-A10) and Eq. (A3), we obtain, after rearrangement,

\[ f(x/L) \equiv \frac{d\mu_{o_{i}}}{d(x/L)} = 4eL \left( \frac{j_{o^-}}{\sigma_{o^-}} - \frac{j_{eh}}{\sigma_{e} + \sigma_{h}} \right) \]  \hspace{1cm} \text{(A11)}

Therefore, the discontinuity in \( \mu_{o_{i}} \) can be avoided if the right-hand side is zero. This result comes directly from Eq. (A3), because even if there is a discontinuity in
$\tilde{\mu}_\text{o} \cdot (x)$ in the ionic channel, it can be countered by a discontinuity in $\tilde{\mu}_\text{e} \cdot (x)$ by fine-tuning the electronic conductivity in the electronic channel for a given ratio of $j_{\text{o}^-}$ to $j_{\text{eh}}$ at the steady state. In general, “impedance matching” by keeping the ratio of electronic conductivity to ionic conductivity the same at the bottleneck and elsewhere will remove the overshoot/undershoot of $\mu_{\text{O}_2}$. (On this point, one finds an analogy in optics in which the impedance is determined by the ratio of magnetic susceptibility to dielectric permittivity.)

For convenience, we now introduce the ionic transference number as $t_i = j_{\text{o}^-} / j_{\text{total}}$ where $j_{\text{total}}$ is the total current density across the electrolyte. (Here and below, $t_i$ should not be confused with grain boundary thickness, which is $t$.) In the SOFC mode, $j_{\text{o}^-}$ and $j_{\text{eh}}$ are in opposite directions and $j_{\text{total}} = j_{\text{o}^-} + j_{\text{eh}} = j_{\text{o}^-} - |j_{\text{eh}}|$. Therefore, Eq. (A11) can be written as

$$f(x/L) = 4eLj_{\text{total}}\left(\frac{t_i}{\sigma_{\text{o}^-}} + \frac{t_i - 1}{\sigma_e + \sigma_h}\right)$$

(A12)

where $t_i - 1$ is the transference number of electrons and holes. In the SOEC mode, $j_{\text{o}^-}$ and $j_{\text{eh}}$ are along the same directions and $j_{\text{total}} = j_{\text{o}^-} + j_{\text{eh}}$. Therefore, Eq. (A11) can be written as

$$f(x/L) = 4eL|j_{\text{total}}|\left(1 - \frac{1}{t_i}\right) \left(\frac{1}{\sigma_e + \sigma_h} - \frac{t_i}{\sigma_{\text{o}^-}}\right)$$

(A13)

where $1 - t_i$ is the transference number of electrons and holes. For completeness, we also give the corresponding form in the open-circuit-voltage (OCV) mode, which is

$$f(x/L) = 4eLj_0\left(\frac{1}{\sigma_{\text{o}^-}} + \frac{1}{\sigma_e + \sigma_h}\right)$$

(A14)

where $j_0 = j_{\text{o}^-} = -j_{\text{eh}}$ denotes the absolute value of the ionic and electronic current
at OCV. Therefore, in all three forms, Eq. (A12-A14), there is only one unknown constant to solve, which is \( t_i \) for Eq. (A12-A13) and \( j_0 \) for Eq. (A14). This is done by satisfying the boundary condition

\[
\int_{\mu_{O_2}}^{\mu_{O_2}} \frac{d\mu_{O_2}}{f(x/L)} = 1 \quad \text{(A15)}
\]

Finally, the oxygen potential distribution can be obtained by integrating \( f(x/L) \) from \( x=0 \) to arbitrary \( x \)

\[
x = L \int_{\mu_{O_2}}^{\mu_{O_2}} \frac{d\mu_{O_2}}{f(x/L)} \quad \text{(A16)}
\]

To allow for special conductivity at special locations, such as grain boundaries, it proves convenient to use a set of discrete coordinates \( x_n \) where the oxygen potential is \( \mu_n \). Instead of Eq. (A15), the boundary condition can now be expressed as

\[
\mu''_{O_2} - \mu'_{O_2} = \sum_{n=0}^{N-1} f(x_n/L) \left( \frac{x_{n+1} - x_n}{L} \right) \quad \text{(A17)}
\]

In the above, \( n \) runs from 0 to \( N \) with 0 corresponding to \( x=0 \) and \( N \) to \( x=L \) in the continuum description. Likewise, instead of Eq. (A16), the oxygen potential distribution can be obtained from

\[
\mu'_{O_2} = \mu''_{O_2} + \sum_{n=0}^{N-1} f(x_n/L) \left( \frac{x_{n+1} - x_n}{L} \right) \quad \text{(A18)}
\]

After obtaining \( \mu_{O_2}(x) \), \( \tilde{\mu}_{O_2}(x) \) and \( \tilde{\mu}(x) \) can be calculated within an integration constant by integrating Eq. (A9-10). (There is only one constant—not two—because the two constants are related to each by Eq. (A3)). Corresponding to this remaining constant is the reference potential of \( \phi \), which of course is arbitrary. In this work, we set it by letting \( \tilde{\mu}_{O_2}(x=0) = 0 \). Lastly, because \( \mu_{O_2} \) is a constant in
YSZ, $-2e\phi$ differs from $\tilde{\mu}_{O^2}$ by an additive constant only, which is again fixed by letting $\tilde{\mu}_{O^2}(x=0) = 0$ in this work. The solution is now complete once $\sigma_i$ is known at every $x_n$. Such information comes from either the local $\mu_{O_2}$ or our knowledge of the microstructure (e.g., the locations of ion-blocking grain boundaries). Specifically, (i) oxygen conductivity is independent of $\mu_{O_2}$ ($\sim 0.03 \Omega^{-1}\text{cm}^{-1}$ at 800 °C in the lattice), and the $\mu_{O_2}$ dependence of electron and hole conductivity is that of Park and Blumenthal$^{25}$ (see conductivity data in Fig. 1); and (ii) the ratio of $\sigma_{O^2}^{\text{GB}}/\sigma_{O^2}^{\text{L}}$ is known from AC impedance spectroscopy (measured at 250-500 °C and extrapolated to 800 °C providing $\sigma_{O^2}^{\text{GB}} = \sigma_{O^2}^{\text{L}}/160$ according to Guo and Maier$^{23,24}$). The ratio could be much lower for some grain boundaries because AC impedance spectroscopy largely overlooks the less conductive grain boundaries.

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**Author contributions**

Y.D. and I.W.C. conceived the project and Y.D. conducted the research. All authors discussed and contributed to writing.

**Competing financial interests**

The authors declare no competing financial interests.
Supplementary information

Potential spikes at transport bottlenecks cause instability of nominally ionic solid electrolytes in electrochemical cells

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Table of content

Supplementary Note 1       Page 2
Supplementary Note 2       Page 5
Supplementary Figure S1    Page 7
Supplementary Figure S2    Page 8
Supplementary Figure S3    Page 9
Supplementary Figure S4    Page 10
Supplementary Figure S5    Page 11
Supplementary Table S1     Page 12
Note 1 Length and time scales required to reach local equilibrium for solid electrolytes

The combined thermodynamic and kinetic analysis in this work relies on the critical though “standard”\textsuperscript{20-22,32} assumption of local equilibrium in the context of irreversible thermodynamics, which requires interacting species to equilibrate at a fine enough length scale and short enough time scale, so that thermodynamic laws still govern their energetics and kinetic laws still govern their transport. Below, we estimate these time and length scales for YSZ and LLZO solid electrolytes under their typical operating conditions.

The time scale for establishing local equilibrium should be smaller than the practical timescale for cell operations, which ranges from hours to days for SOFC/SOEC and batteries. One way to estimate the time scale for reaching local equilibrium is to use the upper and lower limits of stoichiometry under the most oxidizing and most reducing conditions in the operation, and find the time required to transport the species to achieve the stoichiometry change. For YSZ, the oxygen nonstoichiometry $\delta$ of $Y_{0.148}Zr_{0.852}O_{1.926-\delta}$ under the most oxidizing and most reducing conditions in Fig. 4a ($\mu_{O_2}$ of $-5.21$ eV and $0.36$ eV, respectively), is obtained from

$$\delta^2 (\delta + 0.074) \exp \left( \frac{\mu_{O_2}}{2k_B T} \right) = 0.2276 \exp \left( \frac{-3.98 \text{ eV}}{k_B T} \right)$$  \hspace{1cm} (S1)

according to the thermodynamic data in Ref. S1. It gives $\delta$ of 0.001 at $\mu_{O_2} = -5.21$ eV and $3\times10^{-10}$ at $\mu_{O_2} = 0.36$ eV. To fully alter the stoichiometry of an entire 10 μm-thick YSZ membrane over this range (from $3\times10^{-10}$ to 0.001) under an operational current (mostly ionic) of $-1$ A/cm\textsuperscript{2} requires a time of

2
A similar calculation can be performed for LLZO. To achieve a Li stoichiometry change of 0.001 of a 10 μm-thick LLZO membrane at an operational current density (mostly ionic) of −0.1 mA/cm$^2$ requires

\[
\text{current density} = \frac{2 \times (0.001 - 3 \times 10^{-10}) \times 10 \text{ μm} \times 6.10 \text{ g/cm}^3 \times 96485 \text{ C/mol}}{121.7 \text{ g/mol} \times 9.6 \times 10^{-10} \text{ s}} = 9.6 \times 10^{-1} \text{ s}
\]

These times are obviously much shorter than the practical timescale of cell operation.

The length scale over which local equilibrium is established should be much smaller than the size of electrochemical cells and the length scale of the critical microstructure for thermodynamic and kinetic analysis. The shortest of these latter length scales are in the range of tens of μm (such as cell thickness). One way to estimate the length scale to reach local equilibrium is to find the spacing between reacting species, for it is this distance that they must travel before they can react. Since solid electrolytes used for electrochemical cells are all fast ion conductors, ions can travel freely to where an electron/hole is located, and to react, so it is the average spacing between electrons (or holes) that sets the diffusion distance. For YSZ, Park and Blumenthal gave the electron/hole density of \(10^{16-17}/\text{cm}^3\) at 800-1000 °C in Ref. 25. Therefore, every cube of 20-50 nm in size should have one electron (or hole). This
is the average distance that an $\text{O}^{2−}$ (or oxygen vacancy) will random-walk to meet an electron/hole and to react with it to establish local equilibrium. Such distance is short compared to the cell dimensions and the length scale of critical microstructure in YSZ cells.

The diffusion distance estimated above provides us another method to estimate the time required for establishing equilibrium reaction. This is the diffusion time for the $\text{O}^{2−}$ (or oxygen vacancy) to reach an electron/hole. Using

$$t = \frac{(\text{diffusion distance})^2}{6 \times \text{diffusivity}}$$

(S4)

for 3-dimensional random walk with a diffusion distance of 20-50 nm and oxygen diffusivity of $10^{-8}-10^{-7}$ cm$^2$/s at 800 °C$^{52,53}$, we obtain a time of $7 \times 10^{-6}$ s - $4 \times 10^{-4}$ s. Once again, the time is short compared to the typical operational time of a YSZ cell.

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Note 2 Time required for electrons to communicate with an internal precipitate

Because the internal precipitates (O₂ bubbles, voids, or Li or Na metal islands) are all neutral, whereas the ionic species that aggregate to form them (O²⁻, oxygen vacancies, Li⁺, and Na⁺) are charged, the excess charge must be removed by electron or hole transport across the solid electrolyte. If the time required to transport electrons or holes is short compared to the normal parameters of cell operation, then precipitate formation is entirely determined by thermodynamics (i.e., whether the chemical potential of O₂ or Li/Na is high enough) as assumed in our work. Otherwise, the precipitates may not form because additional thermodynamic considerations are needed (a charged entity is energetically costly), or because it is kinetically inhibited by charge transport. Using the conductivity data in Fig. 1 at 800 °C for YSZ and an electronic transference number of 0.0022 for Fig. 4a, and under an operational (mostly ionic) current density of −1 A/cm², we estimate the time required for electron transport in YSZ to neutralize a precipitating oxygen bubble of 100 nm size with 10 atm internal oxygen pressure (hence ideal gas law still valid, with atm converted to Pa), over a 100×100 μm² area that the bubble covers, is

\[
\text{time} = \frac{4 \times \frac{4}{3} \pi \times (50 \text{ nm})^3 \times 10 \text{ atm} \times (96485 \text{ C/mol})}{(8.314 \text{ J K}^{-1} \cdot \text{mol}^{-1}) \times (1073 \text{ K}) \times (1 \text{ A/cm}^2 \times 0.0022)} = 1.0 \times 10^{-7} \text{ s}
\]

Likewise, in a LZZO with a Li⁺ conductivity of ~10⁻⁴ S/cm and an electronic conductivity ~10⁻⁸ S/cm (thus an electronic transference number of 10⁻⁴), under an
operational current density of 0.1 mA/cm$^2$, the time required for electron transport to neutralize a 100 nm Li metal (island) precipitate covering 100×100 μm$^2$ area of LLZO is

\[
\frac{\text{volume}}{\text{density}} \times \frac{\text{density}}{\text{molecular weight}} \times \frac{\text{Faraday constant}}{(\text{current density}) \times (\text{electronic transference number})}
\]

\[
\frac{4}{3} \pi \times (50 \text{ nm})^3 \times \frac{0.534 \text{ g/cm}^3}{6.941 \text{ g/mol}} \times \frac{96485 \text{ C/mol}}{(100^2 \mu \text{m}^2) \times (0.1 \text{ mA/cm}^2 \times 10^{-4})} = 3.9 \text{ s}
\]

Therefore, the time required to deliver electrons/holes to the site of heterophase formation to compensate the charge left by the participating ions is small compared to the operational time of a normal cell.

The same consideration also dictates that this additional current will not disturb the overall current of the cell, i.e., it will not increase the apparent device resistance.
Figure S1 Polycrystalline YSZ electrolyte in SOFC at 1 A/cm² with grain boundaries at ¼L, ½L and ¾L from left and (a) $\sigma_{O^2\text{-}GB}^{\text{Last}} / \sigma_{O^2\text{-}L}^{\text{L}}$ and (b) $\sigma_{O^2\text{-}GB}^{\text{First}} / \sigma_{O^2\text{-}L}^{\text{L}}$ set as $10^{-2}$, $10^{-3}$, or $10^{-4}$, while all other boundaries set at $10^{-2}$. Upper panels: $\mu_{O_2}$ with dashed lines indicating boundary $\mu_{O_1}$ at two electrodes. Middle panels: conductivities of $O^{2-}$, electrons and holes, for $\sigma_{O^{2-}}^{\text{Last/first GB}} / \sigma_{O^{2-}}^{\text{L}} = 10^{-4}$. Lower panels: electrostatic potential $\phi$, electrochemical potentials and chemical potentials of $O^{2-}$ and e, for $\sigma_{O^{2-}}^{\text{Last/first GB}} / \sigma_{O^{2-}}^{\text{L}} = 10^{-4}$. Other conditions: 800 °C with $\mu'_{O_2} = -5.11$ eV ($PO_2=10^{-24}$ atm) at $x=0$, $\mu'_{O_1} = 0.21$ eV ($PO_2=10$ atm) at $x=L$, $L=10$ μm, $r=10$ nm. Ionic vs. electronic transference numbers of the polarized device are 1.0012 vs. 0.0012 for black curve in (a), 1.0011 vs. 0.0011 for red curve in (a), 1.0008 vs. 0.0008 for blue curve in (a), 1.0012 vs. 0.0012 for black curve in (b), 1.0010 vs. 0.0010 for red curve in (b), and 1.0008 vs. 0.0008 for blue curve in (b).
Figure S2 (a) Conductivity data $\sigma_{O^2-}$, $\sigma_e$ and $\sigma_h$ for a hypothetical mixed conductor as a function of $\mu_{O_2}$. $\mu_{O_2}$ distributions were calculated for polycrystalline electrolyte in SOEC at $-1$ A/cm² with grain boundaries at $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$ from left and (b) $\frac{\sigma^\text{Last GB}_{O^2-}}{\sigma^\text{L}_{O^2-}}$ and (c) $\frac{\sigma^\text{First GB}_{O^2-}}{\sigma^\text{L}_{O^2-}}$ set as $10^{-4}$, while all other boundaries set at $10^{-2}$. Dashed lines indicating boundary $\mu_{O_2}$ at two electrodes. Other conditions: 800 °C with $\mu'_{O_2} = -5.11$ eV ($PO_2=10^{-24}$ atm) at $x=0$, $\mu''_{O_2} = 0.21$ eV ($PO_2=10$ atm) at $x=L$, $L=10$ μm, $t=10$ nm. Calculated ionic transference number of the polarized device is 0.610 for (b) and 0.541 for (c).
**Figure S3** Schematics of charge and discharge of (a&c) solid electrolyte interface (SEI) between negative electrode and electrolyte and (b&d) cathode electrolyte interface (CEI) between positive electrode and electrolyte, showing directions of ionic flow $J_{Li^+}$ and electron flow $J_e$ (hole flow in the opposite direction). Also shown are schematic profiles of $\mu_{Li}$ with a jump across a bottleneck in the ionic channel (upper panel) or in the electronic channel (lower panel).
Figure S4 Calculated $\mu_{O_2}$ and $\epsilon\phi$ in polycrystalline YSZ electrolyte in SOEC at −1 A/cm$^2$ with grain boundaries at $\frac{1}{4}L$, $\frac{1}{2}L$ and $\frac{3}{4}L$ from left and (a) all boundaries set at $\sigma_{O_2}^{GB}/\sigma_{O_2}^{L} = 10^{-2}$, (b) first boundary set as $10^{-4}$, (b) last boundary set as $10^{-4}$, (c) first and second boundaries set as $10^{-4}$, (d) second and last boundaries set as $10^{-4}$, and (e) all boundary set as $10^{-4}$. Other conditions: 800 °C with $\mu_{O_2} = -5.11$ eV ($P_{O_2} = 10^{-24}$ atm) at $x=0$, $\mu_{O_2}^L = 0.21$ eV ($P_{O_2} = 10$ atm) at $x=L$, $L=10$ μm, $t=10$ nm. Note: total voltage drop from $x=0$ to $x=L$ increases with the number of severely blocked boundaries.
Figure S5 Calculated distributions of (a) $\mu_{O_2}$ and (b) electronic conductivity $\sigma_e + \sigma_h$ by adding a constant $\sigma_0 = 10^{-7}$, $10^{-6}$, or $10^{-5}$ $\Omega^{-1}\text{cm}^{-1}$ to $\sigma_e + \sigma_h$ at all $\mu_{O_2}$ ranges (from either donor or acceptor dopants). Reference case with $\sigma_0 = 0$ plotted in black for comparison. Conditions: YSZ electrolyte “single crystal” (grain boundary having $\sigma_{O^2}^{\text{GB}} = \sigma_{O^2}^{\text{i}}$) in SOEC at 800 °C and $-1$ A/cm$^2$ with $\mu_{O_2}' = -5.11$ eV ($P_{O_2} = 10^{-24}$ atm) at $x=0$, $\mu_{O_2}'' = 0.21$ eV ($P_{O_2} = 10$ atm) at $x=L$, $L=10$ μm. Note: multiplying $\sigma_e + \sigma_h$ by a constant number, up to 100, at all $\mu_{O_2}$ ranges, does not noticeably change the reference potential profile (black curve) in (a), which is consistent with the calculations of Fig. S2.
### Table S1 Summary of experimental observations

| Materials          | Properties                             | Function | Mode      | Experimental observations                                                                                                                                 |
|--------------------|----------------------------------------|----------|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| YSZ                | Fast O\(^{2-}\) conductor, electronic insulator | Solid electrolyte | SOEC     | Oxygen bubbles and cracks on oxygen-electrode side, preferentially at transverse grain boundaries\(^{4,7-10}\); oxygen electrode delamination; reduction cavities and cracks on hydrogen-electrode side, preferentially at transverse grain boundaries\(^{28,29}\); sharp boundary between reduced and unreduced regions\(^{29,33}\). |
| Beta alumina       | Fast Na\(^{+}\) conductor, electronic insulator | Solid electrolyte | Charging | Na metal precipitation and micro-cracks at transverse grain boundaries, voids and cracks on Na-metal-electrode side; uniform, precipitation layer propagating from Na-side; sharp boundary between reduced and unreduced regions; graphite (current connector for sulfur electrode) imprint.\(^{17-19}\) |
| LLZO               | Fast Li\(^{+}\) conductor, electronic insulator | Solid electrolyte | After cycling | Li metal precipitation at grain boundaries away from Li-metal electrode and without apparent Li dendrite\(^{14-16}\); uniform Li-metal precipitation with constant Li concentration near anode\(^{16}\). |
| SEI on graphite negative electrode | Fast Li\(^{+}\) conductor, electronic insulator | SEI | After cycling | Activity of metallic Li peaks at 20-30 nm below the electrolyte-SEI surface, exceeding boundary values at the surface and in bulk graphite.\(^{38}\) |
| Porous graphene network | Mixed Li\(^{+}\) and electron conductor | Negative electrode | Charging | Li metal precipitation when tested between 3 V and 0.03 V vs. Li/Li\(^{+}\) in half-cell configuration using Li metal reference electrode.\(^{40}\) |
| Li\(_{1.2}\)Ni\(_{0.15}\)Al\(_{0.05}\)O\(_2\) | Mixed Li\(^{+}\) and electron conductor | Positive electrode | Charging | O\(_2\), CO\(_2\) gas evolution.\(^{41,42}\) |