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Breaking OER and CER scaling relations via strain and its relaxation in RuO₂ (101)

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Abstract

Green hydrogen production from abundant water sources is an important component of renewable energy storage. Water oxidation catalysts are typically considered bound by adsorbate scaling relations, limiting their activity for the oxygen evolution reaction (OER) as well as selectivity between OER and the chlorine evolution reaction (CER) that compete in saline water streams. RuO₂ is highly active for both reactions, and recent measurements have shown the OER activity is greater on undercoordinated, high index facets compared to the lowest-energy (110) facet often studied. The growth of such orientations as epitaxial films, however, can result in appreciable strain and potential surface faceting via its relaxation. We find the activity and selectivity towards OER and CER vary with thickness in epitaxial (101) RuO₂ thin films: OER activity decreases 4x as film thickness increases from 8 nm to 48 nm, while CER activity is comparable. Thus, strain and its relaxation can be used to break scaling relationships between OER and CER, highlighting the important role that defects play in selective oxidation processes on RuO₂ in chloride-containing media.

Keywords

strain, defects, oxygen evolution reaction, chlorine evolution reaction, epitaxial thin films

1. Introduction

The slow kinetics of the oxygen evolution reaction (OER) requires efficient catalysts to enable green hydrogen generation via electrolysis of abundant water sources ^{1,2}. Rutile IrO₂ and RuO₂ are exceptionally active OER catalysts ³⁻⁶, and also demonstrate high activity for the chlorine evolution reaction (CER) that competes with the OER during the electrolysis of saline water ⁷. Similarly, OER is a parasitic reaction during the chlor-alkali process ^{8,9}. OER is a four-electron transfer process involving multiple intermediates, namely *O, *OH and *OOH ¹⁰. On the (110) rutile surface ^{11,12}, the binding energies of these OER intermediates scale linearly with one

another due to the common binding of an O atom to the same active (metal) site ^{5,13,14}. Thus, Man et al. introduced the binding energy difference of *OH and *O as a universal descriptor for oxygen evolution activity ⁵. These scaling relationships also fundamentally limit OER activity, as affinity for any given adsorbate cannot be manipulated independently, constraining the performance of any electrocatalyst to a minimum theoretical overpotential of 0.37 V ¹⁵. Similarly, the CER on these surfaces proceed through intermediates (i.e. *OCl) whose binding energies also scale with those of the OER ¹⁶, prohibiting independent tuning of the reaction rates and therefore catalyst selectivity.

Adsorbate scaling relations may be circumvented in active sites with unique geometries, such as those involving adsorbate H-bonding ¹⁷. Calculations suggest such active sites might be induced via doping at the neighboring bridge site on RuO₂ (110) ¹⁷, although more recent calculations suggest H-bonding at the bridge site may be involved in the OER mechanism in the absence of doping as well ¹⁸. Defects on RuO₂ (110) can increase OER activity via strengthening binding to oxygen ^{19,20}, but their presence on both low and high index facets has been predicted to change the reaction mechanism ²¹ and catalyst stability ²² as well. Specifically, defects may trigger a switch from the scaling-bound adsorbate evolution mechanism (AEM) to the lattice oxygen evolution mechanism (LOEM), typically observed to be pH-dependent ^{23,24}. Experimentally, oriented IrO₂ and RuO₂ exhibit greater OER activity on higher index facets ^{25,26}, related to the computed strength of *O binding but possibly also influenced by active site geometry. Theoretical study ²⁷ of RuO₂ has also suggested the CER/OER selectivity may be facet-dependent, perhaps suggesting unique scaling between reaction intermediates.

Strain offers an opportunity to break scaling relations in catalysis ²⁸. Differences in adsorbate binding can arise via changes in electronic structure ^{29,30}, and strain relaxation can induce defects ^{31,32} and surface faceting ³³ with subsequent impact on activity as well. In high surface area systems, strain can be introduced by selective leaching in alloys ³⁴ and generation of core-shell particles ^{35,36}. Given the experimental challenges in controlling and characterizing such systems ³⁷, we take a more fundamental approach ³⁸, where strain can be systematically introduced via epitaxial growth on different substrates ^{39,40} or changing film thickness ^{41,42}.

Here we consider the (101) orientation of RuO₂, more active for OER than the low-index (110) facet ⁴³, incorporating defects via strain relaxation in epitaxial thin films. While the thinnest films (< 10 nm) exhibit a high degree of strain ³³, large lattice mismatch with an *r*-Al₂O₃ or TiO₂ substrate introduces defects upon strain relaxation in thicker films. This relaxation appears to influence the *O binding of surface sites, with thicker films ~4x less active at 1.55 V_{RHE}. While defects have a dramatic impact on OER, the activity in a Cl-containing acidic electrolyte suggests that such defects have minimal effect on CER activity. These findings support that strain and its relaxation can control both activity and selectivity in oxidation reactions.

2. Experimental section

2.1 RuO₂ film growth and characterization

High quality RuO₂ films were grown using the solid-source metal–organic molecular beam epitaxy (SS-MOMBE) technique⁴⁴, with Ru(acac)₃ (97%, Millipore Sigma) sublimed from an effusion cell (E-Science, Inc.) at a temperature of 100°C. Using a radio-frequency inductively coupled oxygen plasma source (Mantis Inc.), atomic oxygen was supplied with an oxygen background pressure of $\sim 5 \times 10^{-6}$ Torr. Films were grown on r-plane sapphire (*r*-Al₂O₃) and TiO₂ substrates (MTI Corporation) at a substrate temperature of 300°C. Film growth was monitored before, during and after growth using reflection high-energy electron diffraction (RHEED, Staib Instruments). Surface roughness was measured using atomic force microscopy (AFM, Bruker) post growth. Structural characterization was carried out using high-resolution X-ray diffraction (HRXRD, Rigaku SmartLab XE), and reciprocal space mapping (RSM). Thickness was determined using grazing incidence x-ray reflectivity (GIXR). Temperature dependent four-probe resistivity measurements were performed in the Van der Pauw geometry (Quantum Design DynaCool Physical Property Measurement System). As shown in Figure S1, the films have atomically-smooth terraces from AFM and changes in strain with film thickness are evident by the observed shift in RuO₂ (101) peaks from HRXRD.

2.2 Experimental testing procedure

Electrochemical measurements³⁸ were conducted with a VSP-300 Biologic® potentiostat at room temperature and ambient pressure. A standard three-electrode setup was comprised of a RuO₂ working electrode, a Pt counter and Ag/AgCl reference electrode in a glass Pine® cell. The RuO₂ film was affixed to a glassy carbon electrode with double-sided copper tape, electrically contacting one edge of the RuO₂ film. Kapton tape defined a circular area of RuO₂ exposed to the electrolyte³⁸ rotated at a constant rate of 900 RPM using a Pine® modulated speed rotator. Electrolytes were prepared with 18.2 MΩ-cm Millipore water, using KOH (Sigma-Aldrich, Semiconductor gr.), H₂SO₄ (Fisher Scientific, ACS gr.), and KCl (Macron, ACS gr.) as noted. Potentio-electrical impedance spectroscopy (PEIS) was performed at the open circuit potential (OCP) with an amplitude of 10 mV. Potentials were corrected for the electrolyte/cell resistance from the high frequency intercept of the real impedance. Discrete points on the Tafel plot were obtained from chronoamperometry holding each potential for 5 min (Figure S2). OER measurements in KOH were carried out in O₂-saturated (Airgas, UHP gr.) electrolyte to fix the equilibrium potential. For comparing OER activity across pH, the concentration of KOH was varied from 0.01 M KOH, 0.1 M KOH, and 1 M KOH. For measurements comparing OER and CER in 0.1 M H₂SO₄, the electrolyte was saturated with N₂. For assessment of charge transfer, 5 mM of K₄Fe(CN)₆·3H₂O (Sigma-Aldrich, ACS gr.) and 5 mM of K₃Fe(CN)₆ (Merck, ACS gr.) were added to Ar-saturated (Airgas, ultrahigh-grade purity) 0.1 M KOH.

3. Results and discussion

We first consider RuO_2 grown on TiO_2 substrates of different orientations by SS-MOMBE³³. As seen previously in literature for epitaxial RuO_2 grown at higher temperatures by pulsed laser deposition (PLD)^{3,25}, we find that the higher surface energy facets^{25,45} are more active than the lowest energy (110) facet for OER (Figure S3), with the (101) facet showing the highest activity.

We next consider RuO_2 (101) films of different thicknesses grown on $r\text{-Al}_2\text{O}_3$ ($\text{RuO}_2/r\text{-Al}_2\text{O}_3$) using SS-MOMBE, where RuO_2 (101) mismatch with $r\text{-Al}_2\text{O}_3$ is greater than its mismatch with TiO_2 (101), exacerbating relaxation-induced effects³³. The resulting films showed a single (101) orientation by XRD and a smooth surface by AFM (Figure S1). Four-point probe measurements show resistivity decreases with increasing film thickness but is sufficiently low for good metallic electron transport³³, with similar metallic-like charge-transfer properties measured in situ via a fast-redox couple (Figure S4(b)). In comparing films from 8 to 48 nm, the increase in full width at half maximum (FWHM) of the rocking curve of the RuO_2 (101) peak suggests a consistent relaxation of strain with increasing film thickness³³.

3.1 Thickness- and substrate-dependent OER

Figure 1(a) (and figure S5(a)) shows OER cyclic voltammetry (CV) for RuO_2 (101)/ $r\text{-Al}_2\text{O}_3$, where activity decreased with increasing RuO_2 film thicknesses, further supported by chronoamperometry (CA) (Figure 1(b), S5(b)). The difference in activity is similar in magnitude to that observed comparing different crystallographic orientations (Figure S3), suggesting strain relaxation via defect formation and/or faceting has an appreciable effect on OER activity.

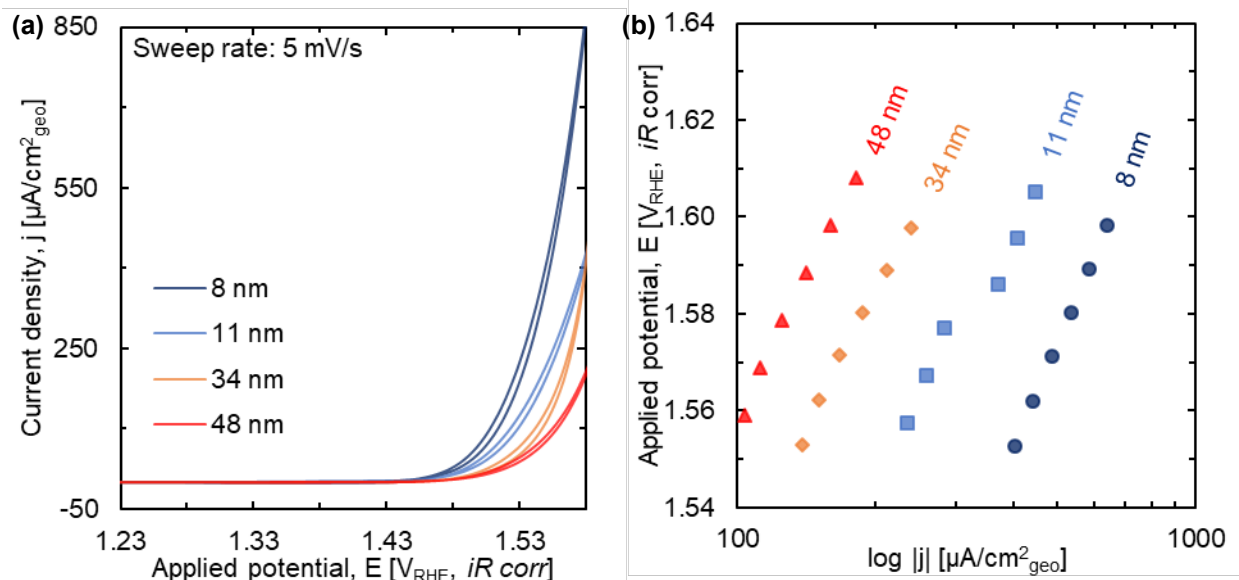


Figure 1: Electrochemical measurements on RuO_2 (101)/ $r\text{-Al}_2\text{O}_3$ films in O_2 -saturated 0.1 M KOH show activity decreases with increasing thickness, both by (a) CV at 5 mV/s and (b) CA (Figure S2), presented as a Tafel plot.

To better understand the origins of thickness impacting OER on RuO_2 , we experimentally assessed the strength of $^*\text{OH}$ and $^*\text{O}$ binding via electroadsorption. Calculations in literature

attribute Ru redox behavior to charge transfer from the electroadsorption of OH ($\text{*H}_2\text{O} \rightarrow \text{*OH} + \text{H}^+ + \text{e}^-$, ~ 1 V vs RHE) and O ($\text{*OH} \rightarrow \text{*O} + \text{H}^+ + \text{e}^-$, ~ 1.4 V vs RHE)^{26,46}. Considering different RuO₂ orientations grown on TiO₂, we see that *O forms at higher applied potentials on the more active (101) facet (Figure 2a), consistent with the calculated higher *O binding energy for this orientation compared to the (110) facet^{25,26}. However, this feature is broader in comparison to the (110) facet, suggesting that a range of local environments might be available on the catalyst surface. Considering the lattice mismatch between (101) RuO₂ and (101) TiO₂ (-1.8% a-axis, +3.0% c-axis), such variation could arise from residual strain or its relaxation via defect formation or faceting. Scanning transmission electron microscopy (STEM) images of the (101) orientation³³ showed no misfit dislocations at the substrate/film interface and an out of plane lattice parameter consistent with strained growth on a TiO₂ substrate, but faceting with the (111) termination along the $[\bar{1}01]$ direction was apparent. This suggests that (101) RuO₂ exhibits strain relaxation accompanying surface faceting.

Surprisingly, the singular broad *O feature for RuO₂ (101) grown on TiO₂ is resolved into two well-defined peaks on *r*-Al₂O₃ grown RuO₂ (101), where greater mismatch may exacerbate relaxation-induced effects. Subtle changes in *O electroadsorption are then observed with changing RuO₂ film thickness on *r*-Al₂O₃, as shown in Figure 2(b). Weighting between *O features at ~ 1.35 V and ~ 1.40 V shifts to stronger electroadsorption with increasing film thicknesses, consistent with calculations in literature showing increased *O binding with defect formation¹⁹. For the thicker films, higher order Ru oxidation at ~ 1.5 V is resolved as reduced OER activity no longer yields overlap in current response between these processes. In contrast, the *OH electroadsorption feature remains broad without notable changes as film thickness increases (Figure S7). Distinctive changes in *O and *OH adsorbate binding (Figure S7), retaining similar charge (Figure S8) are surprising given typical scaling relations⁵, and may indicate unique coordination environments on the surface.

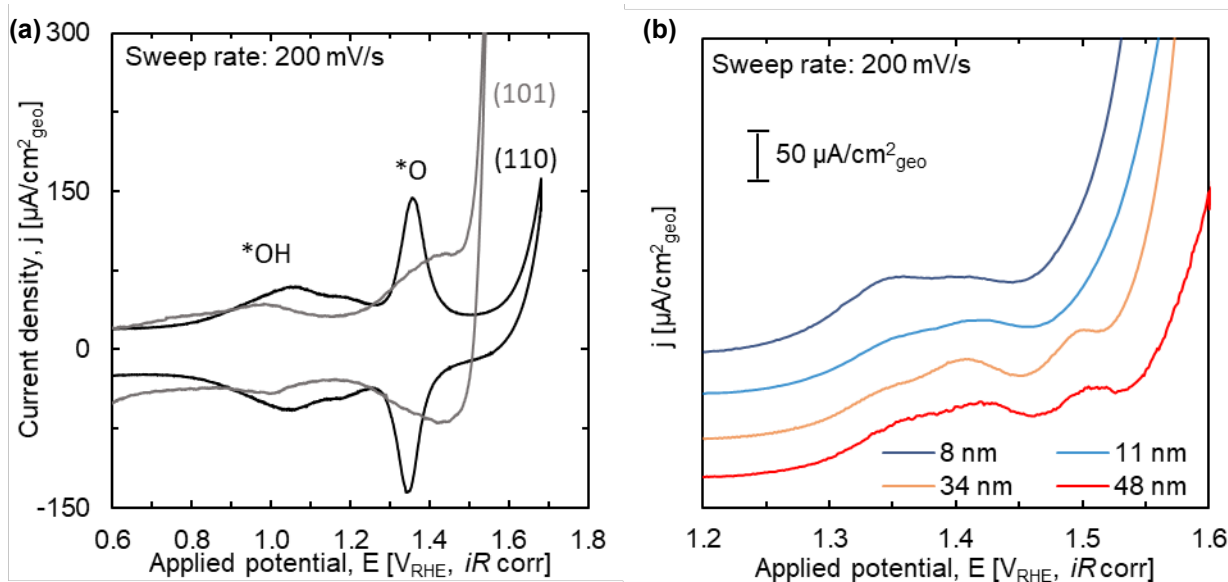


Figure 2: Ru surface redox feature comparison for RuO₂ in N₂ saturated 0.1 M KOH. (a) CV of (101)- and (110)-oriented RuO₂ films (~ 10 nm) grown on TiO₂ substrates with well-defined

features for $^*\text{OH}$ and $^*\text{O}$ electroadsorption and OER activity that differ greatly with crystallographic orientation. (b) Linear sweep voltammetry (LSV) of RuO_2 (101)/ $r\text{-Al}_2\text{O}_3$ films with different thicknesses shows $^*\text{O}$ shifting to higher oxidative potential with increasing film thickness offset for clarity.

To better disentangle the effects of strain and its relaxation, we compared ~ 10 nm thick RuO_2 (101) grown on TiO_2 (101) and $r\text{-Al}_2\text{O}_3$. While the d-spacing for such films is similar at this thickness, the larger lattice mismatch with $r\text{-Al}_2\text{O}_3$ leads to greater defect formation, likely evident from the lack of lattice fringes in XRD (Figure S9). The OER activity is indeed lower for RuO_2 (101) grown on $r\text{-Al}_2\text{O}_3$ relative to TiO_2 (101), consistent with defect formation and/or faceting resulting in lower OER activity.

3.2 Potential changes in OER mechanism

We next assess whether RuO_2 relaxation via defect or facet formation might also lead to changes in OER mechanism, assessed here by the pH dependence of activity. In previous consideration of ~ 25 nm (101)- and (111)-oriented RuO_2 grown by PLD on TiO_2 , online electrochemical mass spectroscopy (OLEMS) measurements did not observe ^{18}O exchange with the lattice on the timescale of measurements, indicating OER proceeded via the AEM mechanism on a wide range of RuO_2 facets²⁵. However, both orientations exhibited pH-dependent OER⁴⁷, attributed to the super-Nernstian shift in Ru redox⁴⁸. In contrast, calculations by Zagalskaya et al. reported that the lattice oxygen evolution mechanism (LOEM) may be competitive at defect sites on RuO_2 (such as metal vacancies)²¹. The rate of LOEM typically increases with solution pH, in contrast to the AEM which is generally considered pH-independent²³. Similar to previous measurements on ~ 25 nm (101) RuO_2 films⁴⁸, we also observe that activity at 1.6 V vs RHE increases with pH for the thickest (48 nm) film (Figure S4(a)), however the thinnest (8 nm) RuO_2 film shows nominally pH-independent OER, where pH-independent OER activity has also been observed on particles⁴⁹. Thus, strain relaxation may lead to mechanistic changes via triggering lattice oxygen involvement or modifying pH-dependent Ru redox, of interest for future studies via ^{18}O labeling.

3.3 Breaking scaling relationship between OER and CER

Having seen that the thickness of (101)-oriented RuO_2 films can impact binding to $^*\text{O}$ as well as the OER activity and its pH dependence, we next consider activity for CER as well. The competitive rates of OER and CER in acidic solution is typically considered bound by scaling relations between the $^*\text{O}$ ($^*\text{OOH}$) and $^*\text{OCl}$ intermediates⁵⁰, with RuO_2 highly active for both reactions without a means to control selectivity between them¹⁶. As in alkaline solutions, OER activity in 0.1 M H_2SO_4 decreases with increasing film thickness (Figure 3). Upon addition of KCl to the electrolyte, exponential oxidative current is observed starting at potentials 0.1-0.2 V below OER onset, attributed to CER with its facile $2e^-$ kinetics^{50,51}, although at higher potentials (e.g. 1.6 V vs RHE) literature notes that both CER and OER co-occur on RuO_2 ⁵². Notably, addition of 100 mM KCl results in comparably high net current for both thicknesses (with CVs for other concentrations of KCl shown in Figure S10). This suggests the relaxation via defect formation/faceting of the thicker film results in greater selectivity towards CER over OER at low overpotentials. For both thin and thick RuO_2 , we observe a reaction order increasing with

applied potential from ~ 1.2 to ~ 1.9 (Figure S11) with respect to $[\text{Cl}^-]$, where reaction orders between 1 and 2 were rationalized by Kuo et al. to arise from potential-dependent $^*\text{OCl}$ coverage over and above the chloride concentration dependence⁵³. Thus, the increased selectivity on thicker RuO_2 (101) may arise from decoupling binding of $^*\text{OCl}$ and $^*\text{O}$ on the surface⁵⁴, otherwise predicted to increase linearly with one another on pristine (110) surfaces¹⁶. Breaking such scaling relations could result from the presence of multiple active sites on relaxed surfaces, unique local coordination and H-binding, or faceting, where different facets have been predicted to have a range of CER selectivity²⁷. Identifying such physical origins is the focus of ongoing work in our lab, as these results suggest defects may offer new opportunities in tailoring selectivity for oxidative reactions.

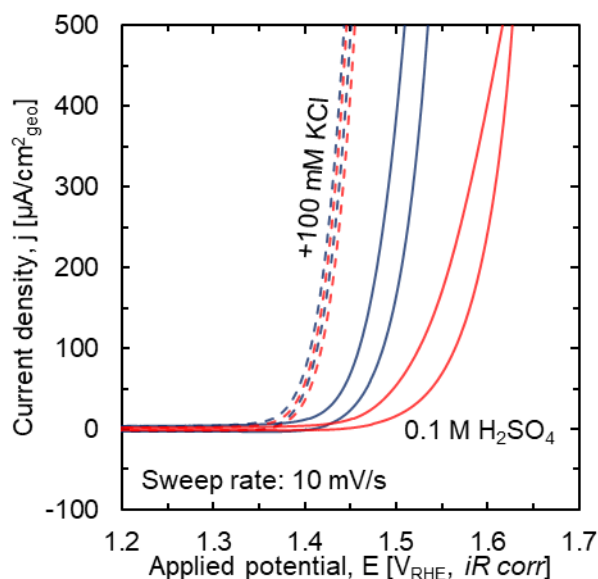


Figure 3: CV trends for 8 nm (blue) and 48 nm (red) $\text{RuO}_2/r\text{-Al}_2\text{O}_3$ (101) in N_2 saturated 0.1 M H_2SO_4 (OER only, solid lines) and in 0.1 M H_2SO_4 + 100 mM KCl (CER+OER, dashed lines). Comparable CER activity but distinct OER activity suggests strain relaxation via defect formation/faceting can break adsorbate scaling relations.

4. Conclusions

In this study, we report a thickness-dependent OER activity for (101)-oriented RuO_2 epitaxial films grown by SS-MOMBE. Increasing thickness of these films has been linked to strain relaxation and surface faceting via STEM³³. Despite films behaving as metals with comparable charge transfer resistance, the OER activity decreased with increasing thickness, attributed to increased strain relaxation via defect formation and faceting. This decrease was commensurate with stronger binding of $^*\text{O}$ to the active sites for increasing film thickness, while binding of $^*\text{OH}$ remained comparable. The OER activity of thicker films increased with pH, observed previously for thick PLD-grown films (e.g. 25 nm)⁴⁸, whereas the thinner more active films studied here (e.g. 8 nm) demonstrated pH independent behavior, indicating mechanistic differences stemming from the nature of the active site induced by strain or its relaxation. Thin RuO_2 with

residual strain is also more active for OER in acid than its thicker, relaxed counterpart, but the films have comparable CER activity in the presence of chloride salts. These findings indicate that strain relaxation and faceting may provide a unique handle to tailor not only activity but also mechanism and selectivity among competitive oxidation reactions.

Data availability

The raw and processed data required associated with the main text are available to download from 10.17632/f9zhbnstht.2. Additional data that support the findings of this study are available from the corresponding author upon reasonable request.

CRedit authorship contribution statement

Prajwal Adiga: Methodology, Investigation, Formal Analysis, Writing – Original Draft, Visualization **Dr. William Nunn:** Resources, Writing – Review and Editing **Cindy Wong:** Investigation, Writing – Review and Editing **Anusha K. Manjeshwar:** Resources, Writing – Review and Editing **Sreejith Nair:** Resources, Writing – Review and Editing **Dr. Bharat Jalan:** Conceptualization, Resources, Writing – Review and Editing, Supervision, Funding acquisition **Dr. Kelsey A. Stoerzinger:** Conceptualization, Methodology, Resources, Writing – Review and Editing, Supervision, Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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