

Photoinduced Mitigation of Solid Oxide Electrolysis Cell Degradation: Light Healing Effect on Oxygen Vacancies

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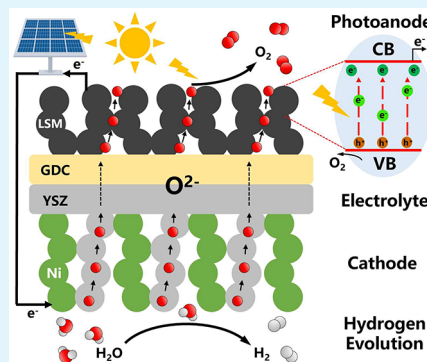
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Supporting Information

ABSTRACT: Hydrogen energy, central to modern energy storage, is promising for use in solid oxide electrolysis cells (SOECs) due to its efficiency and production rate. However, the degradation of SOECs, possibly due to altered oxygen distribution, remains a significant challenge. This study introduces light as a method to stabilize the oxygen distribution and enhance oxygen vacancies, thus countering cell degradation. Using an LSM/GDC/YSZ/Ni-YSZ SOEC, we illuminated the LSM anode and identified a unique “light healing effect” (LHE). This effect, distinct from the photothermal influence, showcased a photoinduced hydrogen yield improvement of 270.1 mmol/m²/h, an 11.7% increase over that in the dark, at 800 °C and 0.8 V. In the stability test, the cell exhibited no degradation and remained stable for 50 h with the LHE, compared to a 10.95% decrease in the dark. We consistently observed the LHE across diverse tests, including tests with traditional anodes (LSM, LSC, and LSCF) and orthogonal experiments ranging from 600 to 800 °C and from 0.8 to 2 V. Our findings suggest that the LHE mechanism may be tied to the creation and buildup of photoinduced oxygen vacancies, which indicates an innovative way to avoid deactivation and even improve the performance of SOEC systems.

KEYWORDS: hydrogen energy, SOEC, solid oxide photoelectrolysis cell, cell degradation, photoinduced oxygen vacancies



Hydrogen is widely regarded as one of the most promising energy storage media of the 21st century, playing a crucial role in the transition toward a low-carbon economy.^{1,2} The electrolysis of water using excess electricity generated from renewable sources, such as solar and wind energy, has garnered significant attention.^{3,4} Various methods of water electrolysis have been researched, including but not limited to alkaline electrolysis, proton-exchange-membrane electrolysis, molten carbonate electrolysis cells, and solid oxide electrolysis cells (SOECs).^{5–8} Among these, SOECs have gained increasing attention in recent years due to their thermodynamic and kinetic advantages at high temperatures, which lead to the highest area-specific rates and energy efficiencies, thereby making them one of the most promising methods for hydrogen production.^{9,10}

However, degradation issues plague the current operational SOECs.^{11–13} Even the reported lower degradation rates are 1.5–5%/kh, which have yet to meet the requirements of large-scale industrialization.^{14,15} Ensuring the stable operation of SOECs over tens of thousands of hours and beyond remains a critical challenge.¹⁶ The most frequently reported and severe issues include cell anode delamination, delamination at the interface of the anode and electrolyte, and problems arising from detrimental secondary phases.^{17,18} The mechanistic explanations suggest that these issues are closely related to the localized oxygen partial pressure within the cell.^{19,20} Under SOEC operation, oxygen accumulates at the anode, and the

discharge of oxygen in a small area at the anode and the junction with the electrolyte creates excessively high local oxygen partial pressures.^{21,22} Excess oxygen can induce the shrinkage and rupture of anode particles, which subsequently leads to cell delamination.²³ Moreover, an abundance of oxygen implies a low concentration of oxygen vacancies, promoting the formation of secondary phases such as SrO and deteriorating the cell performance.²⁴ Additional explanations include cation diffusion and electrolyte secondary phases, all of which are intimately tied to anode degradation based on the oxygen distribution.²⁵

Current solutions primarily focus on material design and cell structure.^{11,13} Material design aims to improve the reaction performance while alleviating electrolysis degradation. For instance, replacing the singular LSM anode with an LSM/YSZ or LSM/GDC composite material allows reaction sites to not be confined within small areas at the anode–electrolyte interface, thereby avoiding oxygen accumulation.²⁶ Using RuO₂ as a catalyst loaded onto the LSM surface enhances

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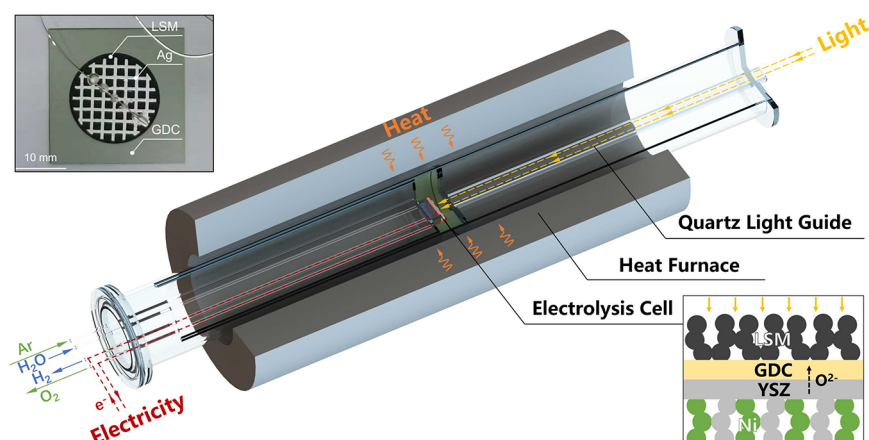


Figure 1. Schematic diagram of the SOPC system for light healing.

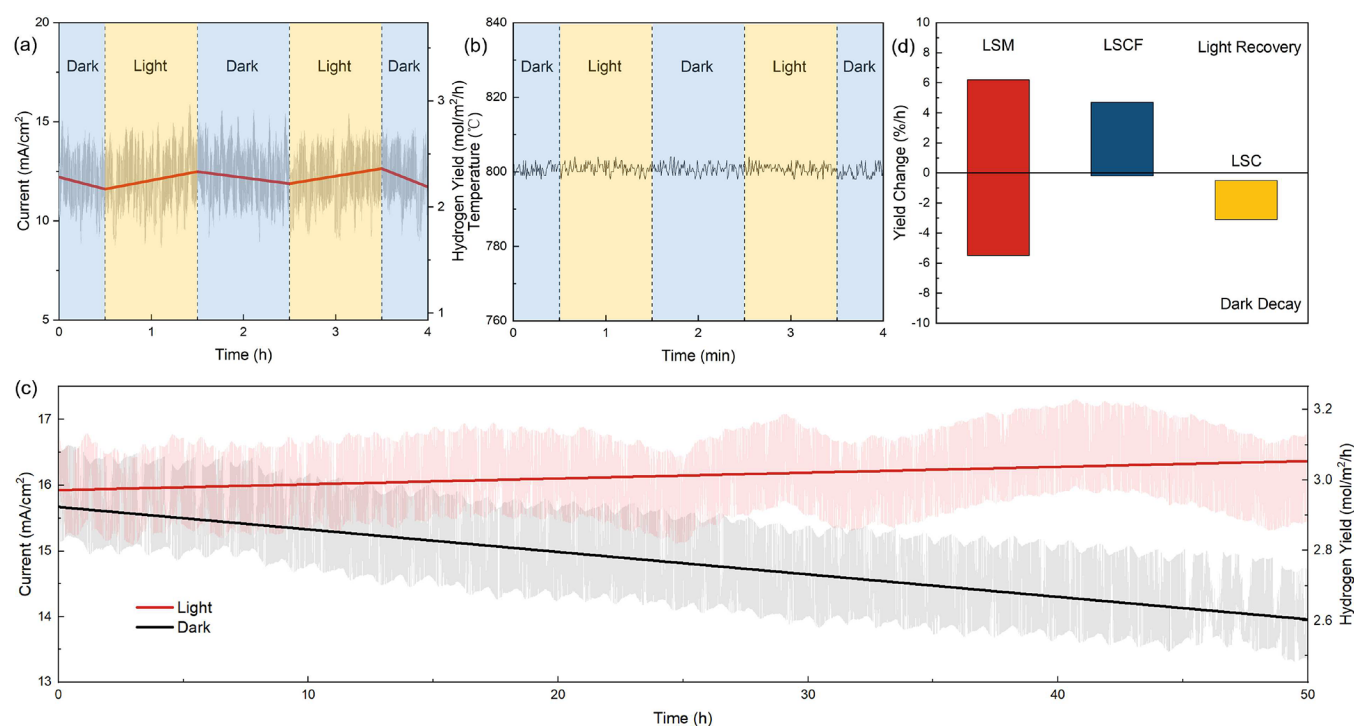


Figure 2. (a) Typical results and (b) temperature of alternate illumination experiments on the LSM anode of the LSM/GDC/YSZ/Ni-YSZ cell. (c) Long-term steady-state experiment. (d) Results for three classical anode materials.

the catalytic performance, reduces the overpotential, and alleviates the high oxygen pressure caused by anode polarization.²⁷ The cell structure is designed to promote the discharge of O₂ gas. The honeycomb-like pores perpendicular to the cell plane enable O₂ gas to be expelled into the atmosphere, preventing local high oxygen pressure.²⁸ Small nanoparticles are used only in the anode functional layer to promote the reaction, while larger particles in the remaining parts ensure smooth gas flow.^{29,30}

Studies in the field of photocatalysis have shown that illumination can cause semiconductor materials to discharge lattice oxygen, generating O₂ gas.^{31–33} In the two-step photothermal chemical cycle, a thermal reaction allows materials to consume oxygen vacancies and react with water to produce hydrogen.^{34,35} Simultaneously, a light reaction enables the material to release oxygen and regenerate oxygen vacancies, thus forming a cycle. This approach of maintaining a

high state of oxygen vacancies in materials through direct illumination is called the photoinduced oxygen vacancy pathway.^{36–38} Moreover, materials rich in oxygen vacancies demonstrate a superior photocatalytic performance compared to their bulk counterparts.^{39,40} This pathway, if applied to SOECs, holds promise for improving the oxygen distribution at the anode, thereby addressing cell degradation issues. However, the method of direct illumination has rarely been reported in SOECs, and the mechanism of light exposure in SOEC cell degradation has scarcely been studied, making this a novel research approach.

In this research, we utilized a conventional SOEC, specifically the LSM/GDC/YSZ/Ni-YSZ cell, to experimentally analyze an illuminated SOEC by directing light onto the LSM anode (Figures 1 and S1). A quartz light guide connected the external light source to the cell's core, ensuring anode illumination. Furthermore, a mesh silver current collector layer

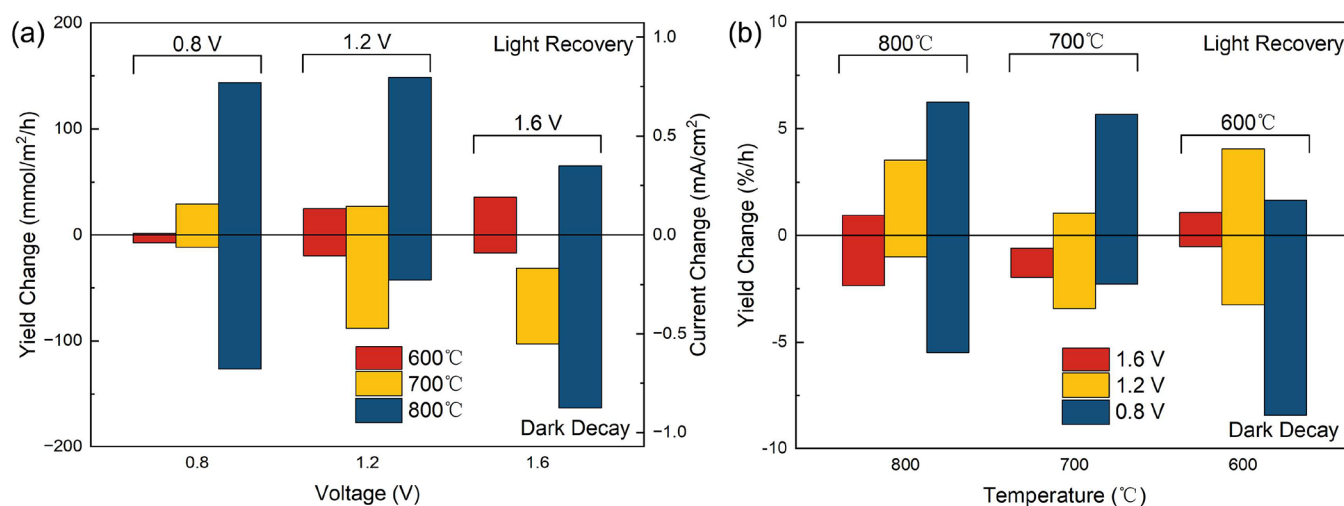


Figure 3. Photoinduced yield change from orthogonal experiments with temperature and voltage: (a) absolute value; (b) percentage relative to the overall yield.

facilitated electrical conduction and allowed for direct anode light exposure.

In our experimental setup, a custom quartz reactor was divided into oxygen and fuel sides featuring a quartz light-guiding column and thermal sealing with high borosilicate glass to accommodate thermal expansion differences. The system was heated to operational temperatures and maintained with precise control, integrating light, thermal, and electrical energies for the reaction process. Light energy was provided by a mercury lamp, while thermal energy came from a heating furnace, gradually increasing from room temperature to the desired level. Electrical energy, which is essential for the reaction, was supplied at a controlled voltage. The gas atmosphere on both sides of the reactor was carefully regulated with water vapor introduced for the fuel side.

Figure 2a reveals the alternating illumination effects on the LSM anode of the LSM/GDC/YSZ/Ni-YSZ cell at a steady 800 °C and 0.8 V. In darkness, the yield decreased incrementally, while light conditions induced a slight yield increase. Interestingly, the transitions between the light and dark did not cause abrupt changes in yield. This “light healing effect” (LHE) denotes the cell’s enhanced performance upon direct anode illumination. We analyzed yield changes linearly under these steady-state conditions, with both dark decay and light recovery representing yield changes over time based on a linear assumption, as elaborated on in the “Data processing” section of the Supporting Information. LHE is quantified in two units to ensure clarity across disciplines, with 1 mol/m²/h of hydrogen being equivalent to 5.36 mA/cm² of current. Within 1 h of the light–dark transition, the dark decay was $-126.5 \text{ mmol/m}^2/\text{h}$ (-5.49% relative to the total yield), and the light recovery was $143.6 \text{ mmol/m}^2/\text{h}$ (6.24%). Light exposure seems not only to counteract cell degradation but also to boost yield.

Figure 2b examines the anode temperature under an alternating illumination. Given that potential temperature fluctuations due to light might influence yield, we monitored the temperature at the light-receiving anode surface. The observed temperature differential was minimal: 800.74 °C in darkness versus 800.88 °C in light—a mere 0.14 °C increase. This negligible temperature variation cannot account for the 11.7% yield shift, thus confirming light’s thermal effect as

inconsequential. This further distinguishes the LHE from light’s thermal effects.

Figure 2c shows the results of a prolonged 50 h steady-state experiment evaluating LHE longevity. The yield exhibited a linear decay over 50 h in darkness, whereas under light, it presented unpredictable fluctuations but generally trended upward. Under dark conditions, the current decreased from an initial value of 15.68 mA/cm^2 to 13.96 mA/cm^2 , a drop of 10.95%. In contrast, under illumination, the current remained stable, increasing slightly from 15.94 to 16.36 mA/cm^2 , a 2.64% improvement. These results indicate that the beneficial impact of the LHE lasts for at least 50 h. Both the alternating light exposure and the sustained response indicate that the phenomenon may extend beyond a mere LHE; light might also play a facilitative role in the reaction. This suggests that the process might involve a combination of electrolysis and photoelectrolysis reactions, corresponding to a novel approach known as the solid oxide photoelectrolysis cell (SOPC).

Finally, Figure 2d assesses the universality of the LHE across three conventional anode materials (LSM, LSCF, and LSC). All three anodes demonstrated LHE. The dark decay values for LSCF and LSC were -0.2% and -3.1% , respectively. Moreover, the light recovery values for LSCF and LSC were $+4.7\%$ and -0.5% , respectively. The LHE appears to be a consistent phenomenon across the tested anode materials.

Alternating illumination experiments on the LSM anode were conducted at varying temperature and voltage settings to assess the behavior of the LHE under diverse operational conditions. Tests spanned three temperature benchmarks (600, 700, and 800 °C) and three voltage levels, including 0.8, 1.2, and 1.6 V, resulting in nine orthogonal experimental combinations.

The absolute yield changes for these nine configurations are shown in Figure 3a. At 600 °C, the dark decays for 0.8, 1.2, and 1.6 V were -7.5 , -19.9 , and $-17 \text{ mmol/m}^2/\text{h}$, respectively, while the corresponding light recoveries were 1.5, 24.7, and $35.5 \text{ mmol/m}^2/\text{h}$. At 700 °C, the dark decays were -11.7 , -88.0 , and $-103.0 \text{ mmol/m}^2/\text{h}$, with light recoveries at 29.0, 27.0, and $-31.4 \text{ mmol/m}^2/\text{h}$. Finally, at 800 °C, the dark decays were -126.5 , -42.6 , and $-163.2 \text{ mmol/m}^2/\text{h}$, contrasting with light recoveries of 143.6, 148.5, and $65.1 \text{ mmol/m}^2/\text{h}$. Remarkably, the impact of the LHE was most

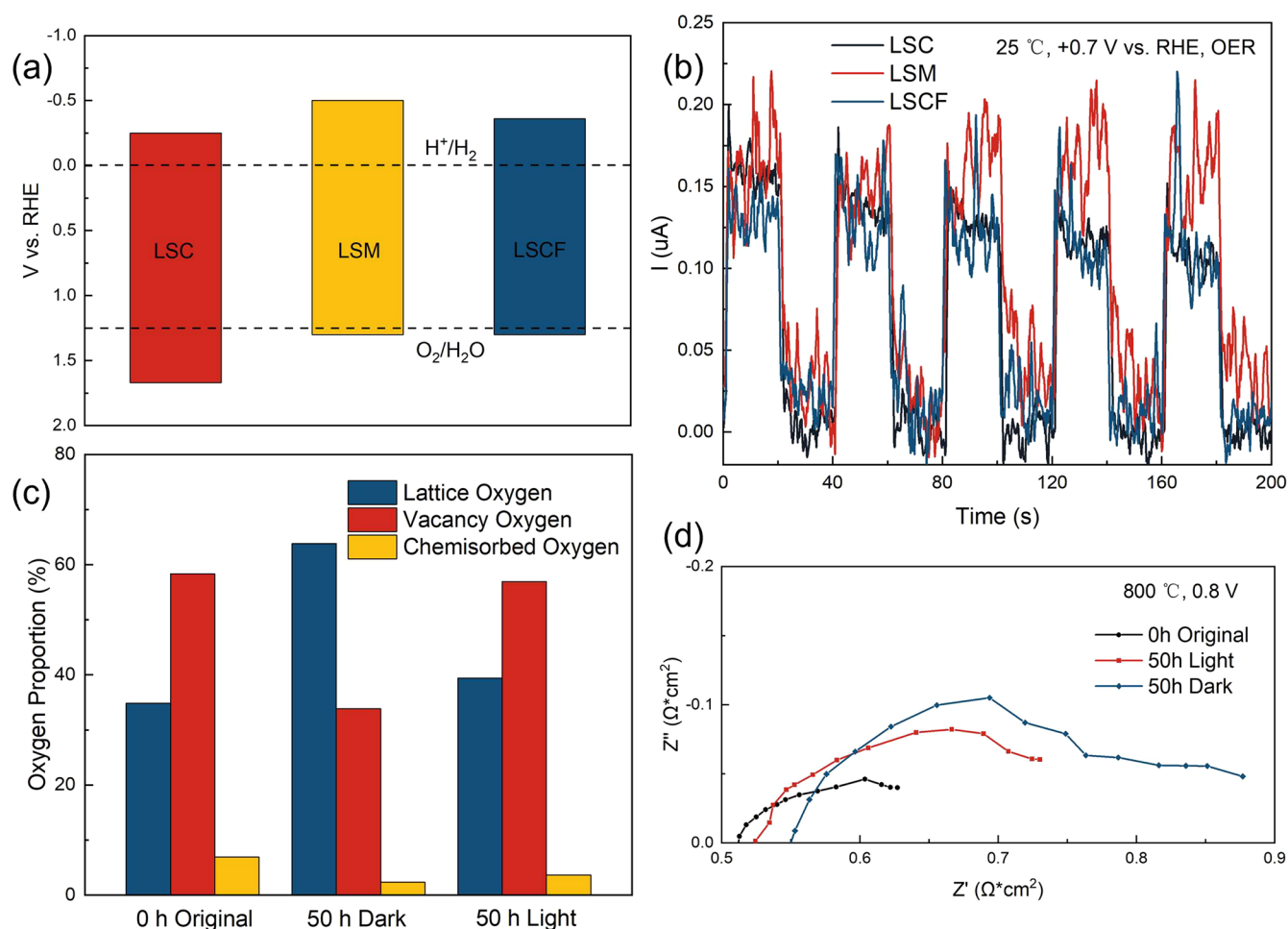


Figure 4. Optical characterization results of LSC, LSM, and LSCF: (a) band structure at room temperature; (b) photocurrent at room temperature. (c) Oxygen proportion in LSM, performed at 800 °C with 0.8 V for cell operation. (d) EIS plots of the cell, performed at 800 °C with 0.8 V for cell operation and voltage-controlled EIS.

pronounced at 800 °C across the voltage spectrum, where the impact was amplified with increasing temperature until reaching this peak.

Insights into the relative yield alterations across the conditions are listed in Figure 3b. For 1.6 V, the dark decays at descending temperatures of 800, 700, and 600 °C were −2.35%, −1.96%, and −0.52% in sequence, while their light recoveries were +0.94%, −0.60%, and +1.08%. At 1.2 V, the dark decays were −1.01%, −3.43%, and −3.25%, with light recoveries of 3.53%, 1.05%, and 4.06%. At 0.8 V, the dark decays were −5.49%, −2.28%, and −8.43%, while the light recoveries reached 6.24%, 5.67%, and 1.66%. From an analysis of these results, the 1.2 V setup demonstrated a superior performance over higher voltage levels, and the 0.8 V configuration excelled over the 1.2 V configuration in relative yield outcomes. The influence of voltage was discernibly greater than that of temperature.

The collective outcomes underscore the LHE's presence across all configurations, with light instigating yield amplification in eight out of nine scenarios. Considering both absolute and relative yield dynamics, it is evident that higher temperatures combined with lower voltages tend to optimize the LHE. The LHE's better performance under warmer conditions likely arises from temperature-induced enhancement of the oxygen-ion-transport rate, which is exponentially more efficient at elevated temperatures. When complemented

with consistent lighting, this augmented transport rate potentially facilitates the systemic dispersion of light action, thereby magnifying the photoinduced hydrogen yields. Conversely, the LHE bias for lower voltages likely emanates from the proportional variance in the electrical energy input. Given that hydrogen production is energy-intensive, a diminished voltage equates to a lower electrical energy contribution. This scenario potentiates heightened relative impacts from both heat and light, culminating in superior photoinduced hydrogen outputs.

Additionally, orthogonal experiments at 500 and 900 °C also exhibited the LHE, although the results were limited due to the extreme temperatures, as detailed in Figure S9.

The characterization results of the electrolysis cell, confirming its operational effectiveness, are provided in Figure S2. The scanning electron microscopy (SEM) image of the LSM/GDC/YSZ/Ni-YSZ cell displays a distinct layered structure. The linear scanning voltammetry (LSV) outcomes revealed equivalent zero points at 800, 700, and 600 °C of 0.795, 0.983, and 1.179 V, which are in line with conventional water-splitting reactions. A close alignment of the current and products was evident, with a quantum ratio of 1.03 between the gas-chromatograph-measured hydrogen and electrochemical-workstation-measured current, indicating minimal side reactions and electronic conduction. The hydrogen–oxygen ratio of 2.11 further confirms the water-splitting reaction.

The material characterization results of LSM, LSC, and LSCF, verifying their aptitude as light-receptive anodes, are presented in Figure S3. The X-ray diffraction patterns for all three materials align with the orthorhombic perovskite structures.⁴¹ The SEM image of LSM highlights spherical nanoparticles ranging from 20 to 90 nm. The X-ray energy-dispersive spectroscopy (EDS) spectrum for LSM confirms a uniform elemental distribution with an atomic composition of 0.695:0.232:1:3.24 La/Sr/Mn/O, consistent with the stoichiometric expectations. The high-resolution transmission electron microscopy (TEM) image showcases lattice fringes corresponding to spacings of 0.379 and 0.380 nm, congruent with the (012) lattice plane of orthorhombic perovskite LSM. The additional material characterizations including TEM, SEM, X-ray photoelectron spectroscopy (XPS), and EDS for LSM, LSC, and LSCF are provided in Figures S7 and S8.

Parts a and b of Figure 4 present the optical characterization results of LSC, LSM, and LSCF, illuminating their suitability as photoresponsive materials; detailed data are available in Figure S4. UV–vis analyses yielded band gaps for LSC, LSM, and LSCF of 1.92, 1.80, and 1.66 eV, respectively, supporting their categorization as direct-band-gap semiconductors.⁴² The Mott–Schottky plots revealed flat-band potentials of −0.86, −1.11, and −0.97 eV for LSC, LSM, and LSCF, respectively, against the Ag/AgCl reference electrode. On the basis potential differentials and prior studies,⁴³ the conduction-band potentials for LSC, LSM, and LSCF were determined to be −0.25, −0.50, and −0.36 eV, respectively. Their associated valence-band potentials were recorded at 1.67, 1.30, and 1.30 eV against the reversible hydrogen electrode. This band structure, as illustrated in Figure 4a, emphasizes their potential in photocatalytic water splitting. Figure 4b displays the noteworthy photocurrents for all of the materials, endorsing their proficiency as photoresponsive materials.

Figure 4c displays the oxygen proportion in LSM, as identified by X-ray photoelectron spectroscopy (XPS), to shed light on the LHE mechanism. The complete data set can be found in Figure S5. Three distinct LSM scenarios were scrutinized: “0 h Original” (prior to reaction), “50 h Dark” (after a 50 h standard reaction), and “50 h Light” (following a 50 h light-enhanced reaction). The adjusted XPS binding energy values based on contamination carbon at 284.8 eV indicated peaks within the range of 536–526 eV corresponding to the O 1s orbital.⁴⁴ This O 1s peak can be further broken down into three subpeaks: 529.4 eV (lattice oxygen, OL), 531.1 eV (vacancy oxygen, OV), and 533.1 eV (chemisorbed oxygen, OC).⁴⁵ For OV, the relative peak areas were 58.3%, 33.9%, and 56.9% for the 0 h Original, 50 h Dark, and 50 h Light scenarios, respectively. Correspondingly, for OL, these values were 34.8%, 63.8%, and 39.4%. It is evident that the 50 h dark period led to a reduction in the OV proportion from 58.3% to 33.9%, while the OL proportion increased from 34.8% to 63.8%. This trend aligns with the recognized mechanism of cell degradation, which is intertwined with oxygen distribution dynamics. Nevertheless, the OV and OL proportions of the 50 h Light sample reverted closely to the original state, resembling the 0 h Original metrics.

These findings suggest that illumination potentially curtails the decline in the number of oxygen vacancies and the proliferation of lattice oxygen. Elevated levels of oxygen vacancies might result in augmented electrical conductivity and catalytic capability, consequently enhancing the SOEC functionality. The contrast between the outcomes from the

50 h Dark and 50 h Light scenarios can potentially be attributed to photoinduced oxygen vacancies. In essence, light exposure creates photoinduced oxygen vacancies, negating the typical cell degradation caused by enriched interface oxygen and emergent secondary phases.

Further substantiation is evident in Figure 4d, which presents electrochemical impedance spectroscopy (EIS) spectra. For the 0 h Original, 50 h Light, and 50 h Dark scenarios, the corresponding high-frequency impedance values were 0.512, 0.524, and 0.550 ohms·cm², and those at 10 Hz (low-frequency) were 0.628, 0.730, and 0.876 ohms·cm². Both the low- and high-frequency impedances displayed a gradual uptrend. Given that cell degradation is intricately linked with oxygen distribution, an impedance increase suggests an enhanced oxygen content, providing indirect evidence that the LHE is dependent on photoinduced oxygen vacancies.

Unlike transient photocatalysis, the formation of photoinduced oxygen vacancies is a more indirect and delayed process, which matches our experimental observation of no instantaneous alterations during light–dark switches. Moreover, with sustained illumination, these photoinduced oxygen vacancies might accumulate in the LSM bulk phase over time. Considering the enormous quantitative difference between photons and material molecules, it is plausible that saturating photoinduced oxygen vacancies is a slow process. This aligns with our experimental findings, which recorded an LHE duration of at least 50 h. The concept of photoinduced oxygen vacancies is supported by our current experimental results, suggesting that the formation and accumulation of these vacancies are plausible mechanisms for the LHE.

SOEC degradation, primarily linked to internal oxygen partial pressure, manifests as mechanical cracks, secondary phase formation, and reduced catalytic activity. Illumination plays a pivotal role in mitigating this degradation by inducing oxygen vacancies. Light-induced vacancies in metal oxides reduce lattice oxygen, thereby decreasing the risks associated with high oxygen partial pressures. These vacancies are generated through electron–hole pair formation and subsequent exciton reduction on metal oxide surfaces, effectively trapping lattice oxygen ions and forming oxygen radicals. This process, facilitated in inert atmospheres, creates vacancies while reducing the material’s oxygen nonstoichiometry, enhancing its stability and performance under operating conditions.

In summary, we successfully developed a photoinduced SOEC system and observed a significant reduction in cell degradation due to direct anode illumination. This effect, known as the light healing effect (LHE), is distinct from light’s thermal properties. Remarkably, during 50 h of illumination, the cell remained stable, and the current even improved by 2.64%, in contrast to a 10.95% decrease in the dark. The LHE was consistent across three conventional anodes—LSM, LSC, and LSCF—and was effective over a range of temperatures (600–800 °C) and voltages (0.8–2 V). Its peak performance, yielding 270.1 mmol/m²/h or an 11.7% improvement, occurred under LSM illumination at 800 °C and 0.8 V. Extensive characterizations confirmed the effectiveness of both the cell and anode materials, while optical tests highlighted their suitability for photoreactions.

The careful investigation into the oxygen distribution and impedance variations under light and dark reactions suggests that the LHE can be attributed to the emergence of photoinduced oxygen vacancies. These vacancies, formed

through illumination, potentially circumvent the typical degradation pathways in cells—mainly those driven by interface oxygen enrichment and the evolution of secondary phases. This novel study offers innovative approaches to counteract SOEC degradation, setting the stage for future enhancements and more extensive adoption of SOEC systems. While we have identified a mechanism linked to photoinduced oxygen vacancies, its complete potential has yet to be realized. Through the optimization of photoelectrode materials, we expect to see significant improvements in the light-induced yields by SOPCs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.3c02754>.

Experimental system, cell preparation, material synthesis, characterization, band structure, data processing, physical picture of a SOPC system, normal cell operation, photoanode material characterizations, optical characterizations, spectrum and intensity of the light source, and experiments at 500 and 900 °C (PDF)

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Author Contributions

D.G. designed and conducted the experiments, analyzed the data, and wrote the manuscript; J.M. conducted part of the experiments; Y.X. conducted part of anode material synthesis and characterizations; J.H. conducted part of the cell construction; M.W. conducted part of the characterizations; C.X. and Y.Z. received funding for the projects and supervised the whole project.

Notes

The authors declare no competing financial interest.

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