INTRODUCTION

Resulting from the recent increase in shale gas production, the supply of ethane has increased more than 15-fold over the past decade in the United States (1). Meanwhile, the distributed nature for shale gas production, coupled with the insufficient infrastructure for ethane transportation, has led to substantial rejection of this valuable chemical feedstock either as a fuel or through flaring. Although thermal cracking is a well-established technology to convert ethane into ethylene, it is only suited for centralized production facilities (e.g., 1 million metric tons/year) because of its high complexity and capital intensity (2). Moreover, the highly endothermic thermal cracking process is energy intensive, resulting in more than 1 metric ton of CO₂ emission per metric ton of ethylene produced. Hence, the existing ethane conversion technology is incapable of addressing the increasing concerns over CO₂ emissions and the changing market conditions in ethane supply.

Among the alternative ethane conversion approaches, oxidative dehydrogenation (ODH) of ethane represents one of the more promising candidates as it catalytically converts ethane in the presence of gaseous oxygen, leading to an exothermic process with potentially higher single-pass ethylene yield at lower operating temperatures (3–6). However, the needs for gaseous O₂ and, hence, an energy-intensive air separation system limit the applicability of conventional ODH at distributed scales (7). This challenge can be mitigated via a chemical looping–ODH approach (CL-ODH) (8–10). In CL-ODH, instead of gaseous oxygen, lattice oxygen from a metal oxide redox catalyst is used to selectively oxidize ethane into ethylene in an ODH step. The reduced redox catalyst is reoxidized with air in a following step, and the active lattice oxygen is replenished. This two-step operation integrates air separation with ODH while avoiding the direct contact between ethane and O₂, rendering a safer and intensified process. A process analysis study indicated that 82% reduction in energy consumption and CO₂ emission can be achieved by CL-ODH when compared to steam cracking (11).

On the basis of the literature published to dates, CL-ODH can be facilitated by the redox catalyst via one of the following two routes. In route 1, a redox catalyst is used to selectively combust hydrogen at ethane thermal cracking temperatures (i.e., >800°C). Yusuf et al. (12–14) and Neal et al. (15) reported that Na₂WO₄ promoted Mn-based oxides in CL-ODH and obtained ethylene yields up to 68% with CO₂ selectivity as low as 1.9% at 850°C. Because of the high operating temperature required, route 1 is only suitable for centralized ethylene production in refractory-lined circulating fluidized beds (11). In route 2, CL-ODH is conducted at temperatures substantially lower than thermal cracking temperatures (≤700°C) via surface activation of ethane in the presence of active oxygen species supplied by the redox catalyst. The lowered operating temperature makes it more suitable for CL-ODH in a modular packed bed for distributed ethane conversion (16). In terms of route 2 redox catalysts, V- and Mo-based oxides, which are commonly used for conventional ODH with oxygen co-feed, have been investigated (17–20). At 500° to 650°C temperature range, steady cycles of 55 to 85% ethylene selectivities were achieved, but ethane conversions were relatively low (7 to 28%). Other than V- and Mo-based catalysts, Gao et al. (21, 22) reported that alkali metal promoted La₅SrₓFeO₄₃ redox catalyst with Ruddlesden-Popper phase and achieved 90% ethylene selectivity at 61% ethane conversion. However, the ethane processing capacity was quite low (0.08 to 0.8 ml of ethane per gram of redox catalyst). Such a narrow operating window limits the practical application of CL-ODH under route 2.

Further improvement of the low-temperature CL-ODH redox catalysts requires better mechanistic understanding. While the mechanistic aspects of conventional, heterogeneous ODH catalysts were extensively studied (23–27), few studies have been conducted to characterize CL-ODH redox catalysts in detail. Specifically, the surface-active phase and the ODH reaction pathway in the absence

**A molten carbonate shell modified perovskite redox catalyst for anaerobic oxidative dehydrogenation of ethane**

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Acceptor-doped, redox-active perovskite oxides such as La₀.₈Sr₀.₂FeO₃ (LSF) are active for ethane oxidation to CO₂ but show poor selectivity to ethylene. This article reports molten Li₂CO₃ as an effective “promoter” to modify LSF for chemical looping–oxidative dehydrogenation (CL-ODH) of ethane. Under the working state, the redox catalyst is composed of a molten Li₂CO₃ layer covering the solid LSF substrate. The molten layer facilitates the transport of active peroxide (O₂²⁻) species formed on LSF while blocking the nonselective sites. Spectroscopy measurements and density functional theory calculations indicate that Fe⁴⁺→Fe³⁺ transition is responsible for the peroxide formation, which results in both exothermic ODH and air reoxidation steps. With >90% ethylene selectivity, up to 59% ethylene yield, and favorable heat of reactions, the core-shell redox catalyst has an excellent potential to be effective for intensified ethane conversion. The mechanistic findings also provide a generalized approach for designing CL-ODH redox catalysts.
of gaseous oxidants are unclear. In this work, we report Li$_2$CO$_3$ as an effective promoter to enhance the CL-ODH selectivity of perovskite oxide–based redox catalysts. Comparing to the previously reported (La/Sr)$_2$FeO$_4$@LiFeO$_2$ redox catalyst, Li$_2$CO$_3$-promoted La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF) demonstrated up to 30 times higher ethane processing capacity while achieving up to 92.2% ethylene selectivity and 63.6% ethane single-pass conversion. Under the working state, the redox catalyst is composed of a molten Li$_2$CO$_3$ layer covering the solid LSF substrate. The molten layer facilitates the transport of active peroxide (O$_2^{2-}$) species formed on LSF while blocking the nonselective sites. Spectroscopy measurements and density functional theory (DFT) calculation indicate that Fe$^{4+}$→Fe$^{3+}$ transition is responsible for the peroxide formation, which results in exothermic ODH and air reoxidation steps.

RESULTS AND DISCUSSION

Figure 1A summarizes the x-ray diffraction (XRD) patterns of the LSF, LSF@Li$_2$CO$_3$ (Li$_2$CO$_3$-coated LSF) samples, and a reference sample, a physical mixture of 20 weight % (wt %) Li$_2$CO$_3$ and 80 wt % LSF. XRD of the physical mixture showed two distinct phases: LSF and Li$_2$CO$_3$. The lower peak intensity of Li$_2$CO$_3$ phase is due to the lower standard XRD intensity of Li$_2$CO$_3$ and its smaller amount. However, the Li$_2$CO$_3$ phase is absent on LSF@Li$_2$CO$_3$ after annealing at 800°C (fig. S1A). This indicates that Li$_2$CO$_3$ becomes amorphous, while LSF remains crystalline, which is supported by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) results (Fig. 1, B and D). In situ XRD under an air flow was conducted on LSF@10Li$_2$CO$_3$ to further validate this at temperatures up to 750°C. Still, only a crystalline phase of LSF was observed (fig. S1B). XPS was conducted on LSF substrate and LSF@Li$_2$CO$_3$ with different loadings. From the surface elemental composition analysis (Fig. 1B), it was determined that both Li$_2$CO$_3$-coated samples have high near-surface coverage of Li (80% in LSF@10Li$_2$CO$_3$ and 82% in LSF@20Li$_2$CO$_3$, oxygen-free basis). Detailed XPS scan of O 1s and C 1s peaks also confirmed that the surface is enriched with Li$_2$CO$_3$-rich species. In Fig. 1C, O 1s scan showed two peaks: a lower binding energy (B.E.) peak at around 528 eV and a higher B.E. peak at around 531 to 532 eV. The lower B.E. peak is ascribed to surface lattice oxygen species (28), and the higher B.E. peak is ascribed to the C=O bond in carbonate species (29). It is clear that Li$_2$CO$_3$ shifts the surface oxygen species from a lattice oxygen–dominating type to a carbonate oxygen–dominating type. The carbonate oxygen peak shifts from 530.8 eV in LSF to 531.5 eV in LSF@20Li$_2$CO$_3$ were ascribed to the surface transition from SrCO$_3$ to Li$_2$CO$_3$ (fig. S2A). C 1s scan also showed that surface is enriched with carbonate species (fig. S2, B and C). TEM was further conducted on cycled LSF@10Li$_2$CO$_3$ ending in oxidation. Figure 1D showed a typical redox catalyst particle. Additional TEM images can be found in the Supplementary Materials (fig. S2D). From the TEM image, a core-shell structured particle was formed. Selected-area electron diffraction (SAED) was conducted on the core and the shell. It is shown that the core material is composed of
crystalline LSF and shell material reflects a primarily amorphous structure. This is consistent with XRD results, where only crystalline LSF phase was observed. On the basis of XPS, SAED, and XRD, the shell material is amorphous Li2CO3. The core-shell structure is further examined with low-energy ion scattering (LEIS), where Fe signal is completely absent on the outer surface of LSF@Li2CO3 (fig. S3A). Differential scanning calorimetry (DSC) was used to measure the physical state of the Li2CO3 amorphous shell at reaction temperatures (650° to 750°C). Melting points of the amorphous surface layer in LSF@Li2CO3 were obtained, and pure Li2CO3 was used as a reference. It was observed that LSF@10Li2CO3 and LSF@20Li2CO3 exhibit melting points between 600° and 700°C, while pure Li2CO3 has a melting point at around 730°C (fig. S3B). The lower melting points observed in LSF@Li2CO3 are likely to be due to melting point depression of the nanoscale shell and/or eutectics of Li2CO3 and a small amount of SrCO3 (30). On the basis of these characterizations, it is concluded that LSF@Li2CO3 exhibits a core-shell structure under reaction temperatures, where core material is LSF and shell material is molten Li2CO3.

To determine the redox catalyst performance, we tested CL-ODH reactions with 12.5 to 80 volume percent (volume %) ethane (balance Ar) in the ODH step and air in the catalyst reoxidation step on LSF and LSF@Li2CO3. The results are summarized in Fig. 2. As is shown in Fig. 2A, blank experiments with inert α-Al2O3 frits showed ethane conversion smaller than 15% at 750°C. In the meantime, LSF substrate exhibited high ethane conversion (>90%) but very low ethylene selectivity (<10%) throughout the conditions tested. Li2CO3 coating on LSF notably increased ethylene selectivity and obtained ~50% ethylene yield between 700° and 750°C. Reaction temperature effect and Li2CO3 loading effects were tested: Higher temperature and lower Li2CO3 loadings lead to higher conversion and lower selectivity. In Fig. 2B, space velocity effect (240 to 960 hour⁻¹) was also studied on LSF@Li2CO3. Higher space velocity leads to lower conversion and higher selectivity. (La/Sr)2FeO4@LiFeO2, reported in our previous study (21), was compared as a reference redox catalyst. Although (La/Sr)2FeO4@LiFeO2 can achieve comparable ethylene selectivity and ethane conversion at very small ethane processing capacities (e.g., 0.075 ml of ethane per gram of catalyst per cycle), it performed poorly at larger ethane processing capacities (6.7 ml of ethane per gram of catalyst per cycle) due to the lack of both selectivity and activity. This shows that LSF@Li2CO3 represents a major improvement in terms of enhancing ethylene yield for practical applications. Note that redox catalyst performance in the ODH step is dynamic with continuous consumption of active lattice oxygen (Fig. 2C). On LSF@10Li2CO3 redox catalyst, ethane conversion decreased from 85 to 43%, and ethylene selectivity stabilized at around 90%. This ethane conversion is higher than both the thermal conversion (7%) and the thermodynamic equilibrium ethane conversion (41%) during the entire ODH step. Because of complete combustion of the hydrogen, as confirmed by negligible H2 signal from both gas chromatography and mass spectrometry results (fig. S4), CL-ODH is no longer subjected to equilibrium limitation of thermal cracking. Lattice oxygen was actively consumed during the reduction step, and about 0.42 wt % lattice oxygen was removed in the first 6 min. Although this oxygen capacity is still relatively small, it remained high catalytic activity throughout the ODH step. One should also note that selective oxidation consumes much less oxygen amount than total oxidation to CO2. To put it into perspective, the 0.42 wt % lattice oxygen capacity in CL-ODH would be equivalent to 1.6 wt % oxygen capacity for chemical looping combustion of ethane after accounting for CO2 formation. Thus, the oxygen-carrying capacity of the redox catalyst, albeit relatively low, fits well with the proposed CL-ODH concept. Effects of ethane concentration were tested as shown in Fig. 2D. It is noted that 50% ethylene yield and 91% ethylene selectivity were still achieved with 80% ethane concentration. Considering that similar performance was achieved at 12.5 to 80 volume % ethane feed, ethane partial pressure of 1 atm or higher would likely yield similar results. The feasibility of using high-concentration ethane feed marks potential advantage compared to conventional ODH with O2 co-feed. Thirty redox cycles were conducted on LSF@10Li2CO3, and the redox catalyst exhibited stable performance (Fig. 2E). Negligible coke formation was observed, as indicated by minimal CO2 formed during the air reoxidation stage (fig. S4).

Thermogravimetric analysis (TGA)–DSC was conducted on LSF substrate with and without carbonate (Fig. 3, A and C). In terms of oxygen storage capacity, TGA indicates 0.5 wt % with and 1.2 wt % without carbonates, these are consistent with the reactive testing results. It is therefore evident that the carbonate shell inhibits lattice oxygen release. Because the oxygen release is contributed by the crystalline LSF phase, in situ XRD under CL-ODH conditions was conducted to better understand the effect of carbonate and degree of reduction. On LSF@Li2CO3 (Fig. 3B), major peaks characteristic of LSF can be observed, and they shift to smaller 2θ (degree) (by ~0.2°, as shown in Fig. 3E) when contacted with ethane. Some minor peaks are present during reaction with ethane, and they are attributed to the Ruddlesden-Popper phase (La/Sr)2FeO4. On the other hand, LSF substrate (Fig. 3D) is reversibly decomposed into La2O3, (La/Sr)2FeO4, and Fe when exposed with ethane at 700°C. Detailed phase assignment can be found in fig. S5. The phase change trend on LSF with and without carbonate, as well as its oxygen capacity and heat of reaction, combined with literature report (31), indicates that the oxygen release is associated with Fe3+→Fe2+ transition in LSF@10Li2CO3, whereas Fe4+/Fe3+→Fe3+/Fe0 in LSf without carbonate. This is further confirmed with Mössbauer spectroscopy results (fig. S6). Oxidized LSF and LSF@10Li2CO3 show similar peak patterns, including Fe3+, Fe4+, and an intermediate Fe oxidation state characteristic of LSF. On the other hand, reduced LSF is composed of LSF (Fe3+), (La/Sr)2FeO4 (Fe3+), and Fe0, whereas reduced LSF@10Li2CO3 shows near exclusively LSF (Fe3+). Meanwhile, DSC in Fig. 3 (A and C) also reveals the differences in the nature of oxygen species participating in the CL-ODH reaction with and without carbonate. With carbonate, the two steps on LSF@10Li2CO3 are both exothermic: −69.5 kJ/mol [O consumed] during the ODH step and −40 kJ/mol [O regenerated] during the reoxidation step based on integration of the heat flow. The exothermic peak in the ODH step is assigned to the reduction of Fe4+ to Fe3+ in LSF@10Li2CO3. The shoulder following the initial peak is likely to be due to a combination of internal mass transfer resistance (in the molten layer and/or LSF), the diminishing driving force for oxygen removal, and the surface kinetics during the later stage of the reduction. Without carbonate, the ODH step is nearly heat neutral, with an exothermic peak followed by an endothermic peak, and the reoxidation step is highly exothermic (−207 kJ/mol [O regenerated]). The exothermic peak in the ODH step for LSf without carbonate corresponds to Fe4+→Fe3+ transition, whereas the endothermic peak is assigned to further reduction of Fe3+ to Fe0. The higher overall exothermicity of LSf without carbonate is due to its nonselective nature, i.e., COx formation leads to increased overall heat release. Table 1 summarizes a
comparison between LSF with and without carbonate. As will be discussed in the later sections, the presence of the molten carbonate layer inhibits deep reduction of LSF by acting as a physical barrier to avoid the direct contact between ethane and LSF surface. The assignment of the ODH active/selective oxygen species will be further discussed in following sections.

To confirm the role of the molten carbonate layer, we also investigated Na$_2$CO$_3$, K$_2$CO$_3$, and Na$_2$CO$_3$-K$_2$CO$_3$ (50-50) mixture as a promoter for LSF. They were selected since Na$_2$CO$_3$ (melting point, 851°C) and K$_2$CO$_3$ (melting point, 891°C) have notably higher melting points than Li$_2$CO$_3$ (melting point, 723°C). Meanwhile, 50 wt % Na$_2$CO$_3$–50 wt % K$_2$CO$_3$ has a melting point of 695°C. As can be seen from Fig. 4A, ethane conversion dropped from 60% (for LSF@Li$_2$CO$_3$) to less than 20% for Na$_2$CO$_3$- and K$_2$CO$_3$-promoted samples. Selectivity also dropped to below 50%. Meanwhile, LSF promoted with Na$_2$CO$_3$-K$_2$CO$_3$ mixture, which is under a molten state

Fig. 2. Reactive testing of LSF@Li$_2$CO$_3$ redox catalysts for ethane ODH. (A) Temperature effect and Li$_2$CO$_3$ loading effect on LSF@Li$_2$CO$_3$: space velocity, 480 hour$^{-1}$. (B) Effect of space velocity on LSF@10Li$_2$CO$_3$ (240 to 960 hour$^{-1}$), with comparison of (La/Sr)$_2$FeO$_4$@LiFeO$_2$ at different space velocity (480 to 3000 hour$^{-1}$) and different ethane feed size (0.05 and 30 ml): temperature, 700°C. (C) Dynamic reaction performance in an ODH step on LSF@10Li$_2$CO$_3$: temperature, 700°C; space velocity, 480 hour$^{-1}$. (D) Ethane concentration effect on LSF@10Li$_2$CO$_3$: temperature, 700°C; space velocity, 480 hour$^{-1}$. (E) Thirty redox cycle tests on LSF@10Li$_2$CO$_3$: temperature, 700°C; space velocity, 480 hour$^{-1}$. 

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at the reaction temperature, exhibited notably higher conversion (29%) and selectivity (75.5%). In general, the activity and selectivity of the alkali metal carbonate–promoted LSF correlate well with the melting point of the carbonate phase. In addition, the presence of a molten phase notably improves the catalytic performance. We note that the melting point of Na$_2$CO$_3$-K$_2$CO$_3$ mixture is similar to that of Li$_2$CO$_3$ coating. However, Li$_2$CO$_3$-promoted LSF is notably more active. This is consistent with the finding by Lunsford and co-workers (32) on molten salt–catalyzed oxidative coupling of methane (with O$_2$ co-feed). It was concluded, in that study, that Li$_2$O$_2$ formed in the presence of O$_2$ is substantially more active than Na$_2$O$_2$ or K$_2$O$_2$. To further quantify the effect of the molten Li$_2$CO$_3$ layer, we performed $^{18}$O$_2$-$^{16}$O$_2$ pulsed isotopic exchange experiments on Li$_2$CO$_3$, LSF, and LSF@Li$_2$CO$_3$ based on the method reported by Bouwmeester et al. (33). The O$_2$ surface exchange was considered as a two-step process, i.e., dissociative surface adsorption and lattice oxygen incorporation. The exchange rate parameters, i.e., overall exchange rate ($R_0$), oxygen adsorption rate ($R_a$), and lattice oxygen incorporation rate ($R_i$), from 500° to 730°C are summarized in fig. S7. The activation energies calculated from Arrhenius fit for each oxygen exchange step are shown in Fig. 4B. On LSF@Li$_2$CO$_3$, an 80% drop in the activation energy for oxygen incorporation, denoted as $E_a(R_i)$, was observed above surface carbonate melting point. This indicates that the formation of the molten Li$_2$CO$_3$ layer substantially

![Fig. 3. Heat of reaction and in situ XRD measurements. (A) TGA-DSC measurement on LSF@10Li$_2$CO$_3$. (B) In situ XRD measurement of LSF@10Li$_2$CO$_3$, phases after the ODH step: LSF (majority) and (La/Sr)$_2$FeO$_4$. (C) TGA-DSC measurement on LSF under 10% ethane/air redox reaction at 700°C. (D) In situ XRD measurement of LSF, phases after the ODH step: La$_2$O$_3$, (La/Sr)$_2$FeO$_4$, and Fe. (E) Enlarged scan on (220) plane of LSF@10Li$_2$CO$_3$ with multiple redox cycles. All the characterizations were performed under 10% ethane/air redox reaction at 700°C.](https://advances.sciencemag.org/)

| Redox catalyst | LSF@10Li$_2$CO$_3$ | LSF |
|----------------|-------------------|-----|
| Oxygen capacity | 0.5 wt %          | 1.2 wt % |
| Ethylene selectivity | 86%              | 6%    |
| Heat of reaction (ODH step) | $-69.5$ kJ/mol [O consumed] | ~Heat neutral |
| Heat of reaction (reoxidation step) | $-40$ kJ/mol [O] | $-207$ kJ/mol [O] |
| Phases after the ODH step | LSF (majority) and (La/Sr)$_2$FeO$_4$ | La$_2$O$_3$, (La/Sr)$_2$FeO$_4$, and Fe |
| Fe oxidation state change | Fe$^{4+}$/Fe$^{3+}$ $\leftrightarrow$ Fe$^{3+}$ | Fe$^{4+}$/Fe$^{3+}$ $\leftrightarrow$ Fe$^{3+}$/Fe$^{2+}$ |
enhances bulk oxygen exchange in LSF@Li2CO3. Moreover, this exchange involves both the Li2CO3 shell and the LSF core. Electrochemical impedance spectroscopy (EIS) measurements were further conducted to quantify the oxygen ionic conductivity and electronic conductivity of pure Li2CO3 (Fig. 4C). It was determined that oxygen ionic conductivity increased with respect to temperature, and about 0.09 S/cm of oxygen ionic conductivity was observed at 720°C (pure Li2CO3 melts at 723°C or 50°C to 100°C higher than that on LSF@Li2CO3). A sharp increase in oxygen ionic conductivity (26-folds from 600°C to 720°C) was observed when approaching the melting point. This indicates that oxygen ionic conductivity can be facilitated by Li2CO3 especially around the melting temperature. It is also noted that electronic conductivity was minimal. This indicates that Li2CO3 can only conduct oxygen ions but is not an electronic conductor. EIS measurement is not specific on the type of anionic oxygen species, i.e., conductivity of O2−, O2−, O2−, O−, and CO42− could all contribute to the total oxygen ionic conductivity.

Fig. 4. Probing the role of the molten carbonate layer. (A) Reaction performance of Na2CO3-, K2CO3-, and Na2CO3-K2CO3–promoted LSF at 700°C. m.p., melting point. (B) Activation energy calculated for oxygen exchange step of Li2CO3, LSF, and LSF@Li2CO3 (500° to 600°C and 650° to 730°C). (C) Oxygen ionic and electronic conductivity of Li2CO3 observed by EIS measurement. (D) Ethane reaction performance on LSF@10Li2CO3 and LSF@20Li2CO3 with and without CO2 co-feed: temperature, 700°C; space velocity, 480 hour−1. (E) (Ethane, O2) co-feed reaction performance on Li2CO3 with and without CO2 co-feed: temperature, 730°C; space velocity, 4000 hour−1. sccm, standard cubic centimeters per minute.
As confirmed by the characterizations above, LSF@Li2CO3 redox catalyst has a core-shell structure with the LSF core carrying the lattice oxygen, and the Li2CO3 shell prevents its direct contact with gaseous ethane. This molten physical barrier between ethane and active oxygen species in LS provides a number of potential reaction pathways (fig. S8A):

(a) ODH occurs between dissolved ethane molecules and active oxygen species within the molten Li2CO3 phase (solution phase reaction);
(b) ODH occurs between dissolved ethane molecules and active oxygen species at the LS surface (reaction at the molten salt–LSF phase boundary); and
(c) Ethane ODH occurs on the outer surface of molten Li2CO3 shell through active oxygen species transported from the LSF core.

For pathways (a) and (b) to be possible, ethane needs to be dissolvable into molten Li2CO3. This was rejected by an ethane/O2 gas switching experiment similar to the report of Lercher and co-workers (34), and it indicates negligible ethane solubility in Li2CO3 (fig. S8B). Therefore, active oxygen species need to be transported from the LSF core, through the molten Li2CO3 layer, to react with ethane on the outer surface. EIS indicates that Li2CO3 conducts oxygen anions but is not electronically conductive. Thus, net flow of O2− (or CO32−) is unlikely since there will not be a net electron conduction to balance the O2− migration. Therefore, oxygen transport through the molten carbonate layer should be in an oxidized form such as peroxide (O22−) or superoxide (O2−). These oxidized oxygen species allows the net transport of oxygen without electronic conductivity. Besides O22− and O2−, gaseous O2, peroxocarbonate (CO32−), or other oxalate ions (C2O42−) are also possible. Release of gaseous O2 is ruled out by O2−-Temperature programmed desorption (O2−-TPD) (fig. S8C). CO32− and C2O42− were also rejected with 13C-nuclear magnetic resonance (NMR) experiments (fig. S8D). As reported and characterized by Devynck and co-workers (35), molten carbonate salts can react with gaseous oxygen to form peroxide. Peng and co-workers (36) reported that CO2 can react with lithium peroxide to form to lithium carbonate. Therefore, formation of peroxide species from carbonate is a reversible reaction, and peroxide formation will be inhibited by excess CO2. CO2 co-feed experiments (10% CO2 + 15% ethane, balance Ar) were conducted on LSF@Li2CO3 for CL-ODH at 700°C. As can be seen from Fig. 4D, CO2 co-feed notably suppressed ethane conversion. A similar trend was observed when co-feeding ethane and O2 to molten Li2CO3 both with and without the presence of CO2. Ethane conversion of 25% was obtained in the absence of CO2 at 730°C but dropped to less than 5% with CO2 co-feed (Fig. 4E). This effect is reversible, and the ethane conversion resumes to its original level when CO2 co-feed is turned off. Similarly, H2 co-feed also inhibited catalyst activity by suppressing peroxide formation (fig. S9A). These results further confirm that peroxide species are likely to be the active oxygen species for CL-ODH.

As have been discussed in Table 1, Fe4+ reduction to Fe3+ in LSF is responsible for supplying the active oxygen species in the CL-ODH reaction. This is further verified with DFT calculations by examining peroxide formation with Fe4+→Fe3+ and Fe3+→Fe2+ redox centers on LS surface. A defect-free LSF (121) surface model was first built, which is one of the more stable surface facets of LaFeO3 family (37). Charge analyses were conducted using the state-of-the-art DDEC06 approach (38) to estimating the trend of Fe oxidation state change. Although the charge values computed from DDEC06 cannot be quantitatively compared to those obtained from the valence bond theory, this method can reliably predict the trend of charge transfer as has been verified in many solid systems (39). As shown in Fig. 5A, a lattice oxygen below the surface was moved to the surface to form a surface O22−. The computed enthalpy change is −0.84 eV, and we correspond it to the Fe4+→Fe3+ transition. In comparison, creation of surface O22− from the Fe3+→Fe2+ transition leads to 0.37-eV enthalpy increase (Fig. 5B). Consistent with experimental data, these DFT results indicate that O22− formation from the reduction of Fe4+ to Fe3+ is energetically favored, whereas further reduction of Fe3+ in LSF is unlikely in the presence of the Li2CO3 molten layer.

![Fig. 5. DFT calculation and proposed reaction pathway. Peroxide formation from (A) Fe4+ to Fe3+ and (B) Fe3+ to Fe2+ during the reduction (ODH) step, with enthalpy changes labeled. Red, blue, green, and purple atoms stand for O, La, Sr, and Fe, respectively. The black atom stands for the selected lattice oxygen that is transported to the surface during the ODH step. The trends of Fe oxidation state change, in terms of net atomic charges, are obtained from charge analysis using the DDEC06 method. (C) Proposed reaction pathways for ODH and reoxidation steps.](https://advances.sciencemag.org/)
Thus, peroxide formation in the ODH step can be written as Eq. 1. As $^{18}$O$_2$-exchange experiments and EIS measurement have shown, oxygen ion transportation is facilitated at carbonate melting point temperature. Thus, the peroxide is transported to the surface, where ODH reaction takes place (Eq. 2)

$$2\text{Fe}^{4+} + 2\text{O}_2^− → 2\text{Fe}^{3+} + \text{O}_2^{2−}$$

$$\text{C}_2\text{H}_6 + \text{O}_2^{2−} → \text{C}_2\text{H}_4 + \text{O}^{2−} + \text{H}_2\text{O}$$

In the air reoxidation step, gaseous oxygen can react with dissolved O$_2^−$ via Eq. 3 to form peroxide.

$$\frac{1}{2}\text{O}_2 + 2\text{O}_2^{2−} → 2\text{O}_2$$

The as-formed peroxide can reoxidize LSF bulk and replenishes its active lattice oxygen species via the reverse reaction of Eq. 1. The reaction pathways for ODH and reoxidation steps are summarized in Fig. 5C. It is noted that molten salt was also shown to be capable of enhancing CO$_2$ absorption for CaO-based sorbents (40). The reactivity of the peroxide species was further reflected with H$_2$-Temperature programmed reduction (H$_2$-TPR) and ethane-TPR on LSF substrate and LSF@Li$_2$CO$_3$. H$_2$-TPR (fig. S9B) indicates that the molten carbonate layer decreases lattice oxygen reducibility of LSF substrate. Moreover, the molten carbonate layer acts as an intermediate to shuttle active oxygen species from the core to the surface. Ethane-TPR indicated that the nonselective oxygen species are minimized with the Li$_2$CO$_3$ layer (fig. S9C). The mechanistic insight obtained is generally applicable to a large family of core-shell redox catalysts. For instance, the redox potential for Co$^{3+}$ / Co$^{4+}$ (1.82 V) is higher than that for Fe$^{3+}$ / Fe$^{4+}$ (0.77 V). Similarly, one would anticipate that Co$^{4+}$-to-Co$^{3+}$ transition would be more facile than Fe$^{4+}$ /Fe$^{3+}$. Li$_2$CO$_3$-promoted La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$, as expected, exhibited notably higher activity and oxygen capacity for CL-ODH. Further increase in Co on the B site, however, can lead to decreased oxygen capacity since reoxidation of the redox catalyst becomes difficult, as can be observed from La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$. On the other hand, LaFeO$_3$ and Ca-doped LaFeO$_3$ have much smaller Fe$^{4+}$/Fe$^{3+}$ than Sr-doped LaFeO$_3$ (41). As expected, they exhibited much lower CL-ODH activity and oxygen capacity. Table S1, which summarizes the reactive performance of a number of core-shell structured redox catalysts, confirmed this effect. We note that while increase in oxygen capacity and oxygen flux is desired, they can lead to unintended consequence of lowered product selectivity. Therefore, a balanced approach needs to be adopted for redox catalyst optimization, as indicated in the current study.

**CONCLUSION**

This study reports a LSF@Li$_2$CO$_3$ as an efficient redox catalyst for CL-ODH. Unlike previously reported redox catalysts, which are typically endothermic during the lattice oxygen-assisted ethane ODH step, the labile oxygen species in LSF@Li$_2$CO$_3$ facilitate exothermic operation in both redox steps as confirmed by TGA-DSC measurements (−69.5 kJ/mol [O] during the ODH step and −40 kJ/mol [O] during the reoxidation step). Up to 92.2% ethylene selectivity and 63.6% ethane conversion were obtained. TEM, XPS, XRD characterizations, and DSC measurement indicate that the redox catalyst is composed of a layer of molten Li$_2$CO$_3$ covering the solid LSF substrate. $^{18}$O$_2$-exchange experiments and EIS indicate that the molten Li$_2$CO$_3$ layer facilitates oxygen shuttling from LSF bulk to the molten carbonate layer surface while blocking the nonselective sites for ethane oxidation. Further investigations of the potential reaction pathways indicate that peroxide species (O$_2^{2−}$) are the most likely active species for CL-ODH. TGA measurements, in situ XRD, and Mössbauer spectroscopy indicate that Fe$^{4+}$ species reduction to Fe$^{3+}$ is responsible for the formation of the active peroxide, which are subsequently transported to the outer surface of the molten Li$_2$CO$_3$ layer for the ODH reaction. The formation of active peroxide via Fe$^{4+}$$→$Fe$^{3+}$ transition is further supported by DFT calculation. With high activity/selectivity and favorable heat of reactions, the LSF@Li$_2$CO$_3$ redox catalyst has excellent potential to be effective for autothermal ethylene production from ethane.

**METHODS**

**Redox catalyst preparation**

Commercial LSF substrate material was purchased from Praxair Surface Technologies (part number: PS-PFeLa313-3D50; lot number: 03-P4993DM). A wet impregnation method was used to synthesize LSF@Li$_2$CO$_3$. Calculated amount of Li$_2$CO$_3$ (ACS reagent; ≥99.0%) was dissolved in 10 ml of deionized water, heated at 50°C, and stirred to form a transparent solution. Then, 10 g of LSF was transferred into the solution, heated, and stirred at 80°C until all the water is vaporized. The dried particles were then transferred into a ceramic sintering boat and sintered in a muffle furnace under air at 800°C for 8 hours.

**Redox catalyst characterization**

Redox catalyst surface and morphology characterizations were conducted with XRD, XPS, TEM, LEIS, Mössbauer spectroscopy, DSC, and Brunauer-Emmett-Teller. Ex situ XRD was conducted with a Rigaku SmartLab x-ray diffractometer to analyze the crystalline phases of redox catalysts. The radiation source was a monochromatic Cu Ka ($\lambda = 0.1542$) with an operating condition at 40 kV and 44 mA. In situ XRD was performed on an Empyrean x-ray diffractometer equipped with an Anton-Paar XRR-900 reactor chamber. Cu Ka ($\lambda = 0.1542$ nm) radiation operating at 45 kV and 40 mA was used to generate XRD patterns. XPS was used to determine the near-surface elemental composition and chemical states. The excitation source was a nonmonochromatic Mg Ka (1254 eV), and the XPS patterns were recorded using a PHOIBOS 150 hemispherical energy analyzer (SPECS GmbH). TEM was recorded on a FEI Talos F200 electron microscope operated at an accelerating voltage of 200 kV. LEIS was conducted at the Surface Analysis Center at the Lehigh University with an ION-TOF Qtacl00 for surface compositional analysis and depth profiling. The detection source is 5-keV Ne$^+$ (1 × 10$^{14}$ cm$^{-2}$ per cycle, 1.5 mm–by–1.5 mm raster), and the sputtering source is 1.0-kV Ar$^+$ (1.0 × 10$^{15}$ cm$^{-2}$ per cycle, 2 mm–by–2 mm raster). Mössbauer spectroscopy was conducted in the Dalian Institute of Chemical Physics. $^{57}$Fe Mössbauer spectra were collected at room temperature (constant accelerations mode) using $^{57}$Co $\gamma$-quantum source in the Rh matrix. All spectra were computer-fitted with a least-squares fitting procedure to a Lorentzian shape. The isomer shifts were fit with respect to α-Fe at room temperature. DSC measurement was conducted with a thermogravimetric analyzer (TGA, Q600, TA Instruments) instrument. Brunauer-Emmett-Teller surface areas were obtained with a Micromeritics ASAP 2020 accelerated
surface area and porosity system via a multipoint physical adsorption measurement.

**Oxygen ionic and electronic conductivity measurement**

EIS was conducted to measure the oxygen ionic and electronic conductivity of Li$_2$CO$_3$. Dense Li$_2$CO$_3$ pellet was prepared and filled into an 11-mm–inner diameter (ID) Al$_2$O$_3$ short tube. Silver ink (Fuel Cell Materials Co.) was applied to Li$_2$CO$_3$ on both ends with silver wires used as lead wire. One side of the tube was exposed to flowing 3 volume % H$_2$O containing H$_2$, the other side to flowing dry air. Open-circuit voltage and AC impedance were measured from 600° to 720°C using Metrohm Autolab. Impedance was collected over a frequency range from 0.1 Hz to 1 MHz with an AC perturbation of 10 mV.

**Oxygen exchange rate measurement**

Oxygen exchange rates were measured using $^{18}$O$_2$-exchange experiments with a pulse experiment setup. This methodology was first reported by Bouwmeester et al. (33), and detailed theories and derivations can be found in (33). The carrier gas was a constant flow of 10% $^{16}$O$_2$ (50 ml/min, balance Ar), and 1 ml of 10% $^{18}$O$_2$ (balance He) was pulsed onto samples for oxygen isotopic exchange. Three isotopes were obtained after the exchange: $^{16}$O$_2$, $^{16}$O$^{18}$O, and $^{18}$O$_2$. They were monitored and quantified with a downstream quadrupole mass spectrometer (QMS; MKS Cirrus II) by taking the integration of the characteristic peak mass 32, mass 34, and mass 36, respectively. More detailed experimental methods were reported in (22).

**$^{13}$C-NMR measurement**

NMR measurements were conducted in the Molecular Education, Technology, and Research Innovation Center at the North Carolina (NC) State University. $^{13}$C-NMR was collected on a 700-MHz Bruker NEO or Avance III spectrometer with TCI Cryoprobe. Before analysis, cycled LSFeLi$_2$CO$_3$ (ended in oxidation) was quenched in room-temperature deionized water. Then, the powder/water mixture was sonicated and centrifuged. This is to allow carbon-containing species to dissolve for NMR analysis. Meanwhile, a standard Li$_2$CO$_3$ solution was also prepared as a control sample.

**Reactive performance testing**

Reactivity test was conducted in a fixed bed quartz U-tube reactor (ID, 1/8 inches or 3.175 mm). Redox catalysts (4.5 to 5 g) were loaded into the reactor, and silicon carbide particles were placed on both sides of the reactor to reduce the void space. Ethane (12.5 to 80%; balance Ar) was injected into the reactor, with a flow rate of 20 to 80 ml/min. Product distributions were monitored with both downstream QMS and gas chromatography. Detailed methodologies for QMS quantification, coke formation, and oxygen capacity calculations were described in (21).

**Computational tools**

First-principles simulations were performed at the DFT level. All simulations were implemented using the Vienna Ab initio Simulation Package with the frozen-core all-electron projector augmented wave model with Perdew-Burke-Ernzerhof functions used to describe the interactions between core and electrons. The kinetic cutoff energy was set to 450 eV for the plane wave expansion of the electronic wave function. The convergence criterions of force and energy were set as 0.01 eV Å$^{-1}$ and 10$^{-5}$ eV, respectively. A 6 × 4 × 6 Gamma-centered k-point grid was chosen for the LSF unit cell. The strong on-site coulomb interaction on the d-orbital electrons on the Fe sites was treated with the generalized gradient approximation (GGA) + U approach. We adopted $U_{eff} = 4$ eV for Hund’s exchange interaction, which have been proven to give reasonable predictions of both geometric and electronic structures in previous works (42). Charge distribution was examined with the DDEC06 method, which is a refinement of the Density Derived Electrostatic and Chemical (DDEC) approach (38).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/17/eaa9339/DC1

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