# Chlorine-Doped Perovskite Oxide: A Platinum-Free Cathode for Dye-Sensitized Solar Cells

Wei Wang,<sup>†</sup> Richard Tran,<sup>‡</sup> Jifa Qu,<sup>§</sup> Yu Liu,<sup>†</sup> Chi Chen,<sup>‡</sup><sup>®</sup> Meigui Xu,<sup>§</sup> Yubo Chen,<sup>||</sup> Shyue Ping Ong,<sup>‡</sup><sup>®</sup> Lianzhou Wang,<sup>⊥</sup><sup>®</sup> Wei Zhou,<sup>§</sup><sup>®</sup> and Zongping Shao<sup>\*,†,§</sup><sup>®</sup>

<sup>†</sup>WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, Western Australia 6845, Australia

<sup>‡</sup>Department of NanoEngineering, University of California San Diego, 9500 Gilman Dr, Mail Code 0448, La Jolla, California 92093-0448, United States

<sup>§</sup>State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China

School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore <sup>1</sup>School of Chemical Engineering and AIBN, The University of Queensland, St Lucia, Brisbane, Queensland 4072, Australia

## Supporting Information

**ABSTRACT:** Triiodide/iodide  $(I_3^-/I^-)$  redox couple-mediated solar cells, batteries, and electrochromic devices require highly efficient and stable electrocatalysts for  $I_3^-$  reduction reaction (IRR) to overcome performance limitations, whereas the widely used platinum (Pt) cathode for IRR has limitations of high price and unfavorable durability. In this work, we present a halogen element (chlorine) doping strategy to design low-cost perovskite-type electrocatalysts with enhanced IRR activity and stability. The dye-sensitized solar cell (DSSC) assembled by the  $LaFeO_{2.965-\delta}Cl_{0.035}$  cathode delivers an attractive power conversion efficiency (PCE) of 11.4% with a remarkable PCE enhancement factor of 23% compared with Pt, which is higher than most of the reported non-Pt DSSC cathodes. Attractively, LaFeO<sub>2.965-δ</sub>Cl<sub>0.035</sub> displays superior IRR activity/stability and structural stability in the I3-/I-based electrolyte



compared to pristine LaFeO<sub>3</sub> because chlorine doping facilitates the creation of oxygen vacancies (active sites) and enhances surface acidity simultaneously. This study provides a new way for designing outstanding IRR electrocatalysts, which could be applied to many redox couple-mediated photo/electrochemical devices.

KEYWORDS: dye-sensitized solar cell, perovskite oxide, cathode, anion doping, electrocatalyst

#### 1. INTRODUCTION

High-efficiency conversion of sunlight energy to electric power is a promising route to address the energy shortage problem. Among the various sunlight-to-electricity systems, dyesensitized solar cells (DSSCs) have received increasing interest because of the relatively high power conversion efficiency (PCE) and ease of fabrication.<sup>1-4</sup> A DSSC typically consists of a dye sensitizer, a TiO<sub>2</sub>-based photoanode, an  $I_3^-/I^-$ -based electrolyte, and a platinum (Pt) cathode (counter electrode, CE). The cathode is a crucial component that governs the triiodide  $(I_3^-)$  reduction reaction to  $I^-$  (IRR) and determines the PCE partly. An excellent cathode should exhibit superior activity and durability for IRR. To date, Pt is the most commonly used cathode. Although it shows favorable activity for IRR, the high cost, low abundance, and inferior stability (decomposed to PtI<sub>4</sub>) seriously restricts its large-scale application in practical DSSCs.<sup>5</sup> Thus, cheap non-Pt alternatives with superior activity and stability are highly sought after as DSSC cathodes. Thus, tremendous investigations have been conducted to substitute Pt with more abundant and cheaper electrocatalysts such as carbons, metal sulfides/selenides, non-Pt metals, and metal oxides.<sup>6-10</sup>

Carbon materials are extensively investigated as Pt-free cathodes in DSSCs because of the superior conductivity and high surface area. Nevertheless, it is still a big challenge to exploit carbon materials with comparable or higher IRR activities than the Pt cathode.<sup>11,12</sup> Doped graphene with tailored morphology is one of the most attractive carbon-based cathodes for DSSCs up to now,<sup>13-15</sup> which, however, suffers from toxic raw materials and/or complex synthesis processes. Although metal sulfides show favorable IRR activity, the low conductivity and inferior chemical durability greatly limit the practical use. As to metallic catalysts, some non-Pt metal-based

Received: May 7, 2019 Accepted: September 5, 2019 Published: September 5, 2019 cathodes were also exploited, however, these catalysts still suffered from poor stability in the  $I_3^-/I^-$ -based electrolyte.<sup>5</sup>

Metal oxides have received increasing attention as alternative Pt-free DSSC cathodes because of the superior performance, low price, large choices, and easy synthesis.<sup>16–18</sup> In particular, the introduction of oxygen vacancies into the oxide lattice may significantly increase their activity for IRR.<sup>17</sup> In addition, the doping of oxygen site in oxides with halogen could create a strong metal—halogen interaction, which could effectively improve the durability of the metal oxide by reducing the corrosion by electrolyte solution.<sup>19,20</sup> However, it is difficult to create a large concentration of oxygen vacancies in simple oxides.

Perovskite oxides  $(ABO_3)$  are a type of complex oxides with a defined lattice structure, in which A/B/O sites can all be doped with other elements without affecting the basic lattice structure, so as to create various materials with tunable and different properties.<sup>21,22</sup> In particular, the doping of A-site by a cation with a low oxidation state resulted in the creation of oxygen vacancy in the perovskite for electrical neutrality, which may have a big influence on its catalytic activity for redox reactions.<sup>21</sup> Indeed, many perovskite oxides have turned out to be excellent electrocatalysts for oxygen evolution/reduction reaction (OER/ORR) at room temperature.<sup>23-26</sup> Some perovskite oxides show activity even better than the benchmark precious metal-based catalysts.<sup>23,25</sup> More recently, we have demonstrated that defective perovskite oxides are also excellent catalysts for promoting free radical formation from peroxymonosulfate for wastewater treatment.<sup>27,28</sup> For all these applications, the doping in cation sites is applied to tune the oxygen vacancy amount or the valence state of B-site cation(s) and, consequently, the activity.

Herein, for the first time, we report chlorine doping on the oxygen site as a new strategy to design and develop perovskitebased electrocatalysts as alternative Pt-free cathodes in DSSCs, demonstrating both high activity and outstanding stability. Specifically, LaFeO<sub>2.965- $\delta$ </sub>Cl<sub>0.035</sub> with an orthorhombic structure was designed and synthesized. The chlorine doping in the oxygen site induced the formation of rich oxygen vacancies in the LaFeO<sub>3</sub> (LF) lattice and a reduction in the oxidation state of the B-site metal (Fe), consequently altering LF from a poor IRR electrocatalyst into a highly active cathode in DSSCs. The reduced oxidation state of Fe in Cl-doped LF was both demonstrated by experimental study and density functional theory (DFT) calculations. Optimized DSSCs with the LaFeO<sub>2.965-6</sub>Cl<sub>0.035</sub>-based cathode displayed a superior PCE of 11.4% under simulated sunlight illumination (AM 1.5 G, 100 mW cm<sup>-2</sup>), which was 23% higher than the Pt-based DSSC (9.28%). In addition,  $LaFeO_{2.965-\delta}Cl_{0.035}$  showed a much better operational durability than the undoped LF and Pt cathodes.

#### 2. EXPERIMENTAL SECTION

**2.1. Material Synthesis.** LF and various Cl-doped LF were prepared by an ethylenediaminetetraacetic acid–citric acid (EDTA–CA) complexing route. Different ratios of  $La(NO_3)_3.6H_2O$ ,  $LaCl_3.7H_2O$ , and  $Fe(NO_3)_3.9H_2O$  were mixed in deionized water. Complexing agents (EDTA and CA) were then added with molar ratios of 1:1 and 2:1 as compared with the amount of the total metal ions. The pH of the as-obtained solution was kept at 6 by using aqueous ammonia solution to complete the complexation process. After heating at 150 °C under continuous stirring, a transparent gel was obtained and further heated at 250 °C in air for 5 h to obtain a black precursor, which was then calcined at 800 °C in air for 5 h.

Commercial P25-TiO2 and synthesized TiO2 microspheres were applied as the photoanodes for DSSCs in this study. The physical properties of P25-TiO<sub>2</sub> are displayed in Figure S1 (Supporting Information), and mixed TiO<sub>2</sub> phases (anatase and rutile) were found in P25-TiO<sub>2</sub> with a Brunauer-Emmett-Teller (BET) specific surface area of ~60 m<sup>2</sup> g<sup>-1</sup>. TiO<sub>2</sub> microspheres were synthesized by a solvothermal route.<sup>29</sup> More specifically, 1 mL of tetrabutyl titanate was added to 50 mL of acetic acid with polyethylene pyrrole (PVP, K-30, 0.24 g) under stirring. After a solvothermal treatment at 150 °C for 24 h, the products washed by ethanol and water were sintered at 400 °C in air for 2 h to get TiO<sub>2</sub> microspheres as photoanodes for DSSCs. The physical properties of the TiO<sub>2</sub> microspheres are displayed in Figure S2 (Supporting Information), and mixed phases of anatase  $TiO_2$  and  $TiO_2(B)$  were observed in  $TiO_2$  microspheres with a BET specific surface area of  $\sim 150 \text{ m}^2 \text{ g}^{-1}$  and an average diameter of  $2-3 \ \mu m$ 

2.2. DSSC Assemblage and Solar Cell Tests. The F-doped SnO<sub>2</sub> (FTO) conducting glass (8  $\Omega$  cm<sup>-2</sup>, GreatCell Solar Limited, Australia) was washed with acetone, deionized water, and ethanol under ultrasonic vibration. To suppress the conductivity limitation of the cathode film, the perovskites were mixed with commercial highly conductive carbon black (CB) or multiwalled carbon nanotubes (MWCNTs) at a mass ratio of 1:1 by ultrasonic dispersion method in the case of FTO-electrode data (DSSC device performance). The Xray diffraction (XRD) patterns, nitrogen adsorption/desorption isotherm patterns, and transmission electron microscopy (TEM) images of MWCNTs and CB are displayed in Figure S3 (Supporting Information). For cathode film preparation, a perovskite-carbon mixed slurry was prepared by ultrasonication with the ethanol solvent. The spray-deposited cathode films were then annealed at 400 °C in the air for 0.5 h to ensure good adhesion between the cathode film and the FTO glass. Based on the thermogravimetric results of LFCl-2/CB (1:1, by weight) composite and CB (Figure S4a, Supporting Information), almost no weight loss was observed for LFCl-2/CB and CB samples at 400 °C, suggesting the presence of carbon in the LFCl-2/CB composite after calcination at 400 °C. The XRD patterns of the LFCl-2/CB composite before and after calcination at 400 °C are also provided (Figure S4b, Supporting Information). In addition to the peaks of perovskite oxides, the XRD peaks of CB were also found, confirming the presence of carbon in the LFCl-2/CB composite after calcination. In addition, based on the TEM-energy dispersive X-ray spectroscopy (EDX) mapping images shown in Figure S5 (Supporting Information), all elements including La, Fe, Cl, O, and C were found for the LFCl-2/CB composite before and after calcination at 400 °C. All of the above results confirmed the presence of carbon in the LFCl-2/CB composite after calcination at 400 °C. The thickness of the cathode layer was around 30  $\mu$ m based on the cross-sectional scanning electron microscopy (SEM) image (Figure S6, Supporting Information).

For the photoanode preparation, 40 mM TiCl<sub>4</sub>-H<sub>2</sub>O solution was used to treat FTO glass at 70 °C for 0.5 h, and then the FTO glass was annealed at 400 °C for 0.5 h in air. A slurry of TiO<sub>2</sub> nanocrystalline layer with improved light-harvesting capability for spin-coating was synthesized by diluting the commercial TiO<sub>2</sub> paste (18NR-T, GreatCell Solar Limited, Australia) with ethanol (10 wt % vs 90 wt %). This TiO<sub>2</sub> layer was then spin-coated onto the TiCl<sub>4</sub>treated FTO at 2000 rpm for 0.5 min (4 times) and then calcined at 400 °C for 0.5 h. The volume of nanocrystalline TiO2/ethanol suspension for spin coating was precisely controlled at 50  $\mu$ L each time. The thickness of this  $\text{TiO}_2$  layer was around 8  $\mu$ m based on the cross-sectional SEM image (Figure S7, Supporting Information). The photoanode suspension (0.5 g TiO<sub>2</sub> microsphere or P25-TiO<sub>2</sub> powder in 10 mL ethanol with 5 wt % PVP) was spray-deposited on the surface of nanocrystalline TiO<sub>2</sub> and then calcined at 400 °C in the air for 0.5 h, and the thickness of this layer was around 30  $\mu m$ (Figure S7, Supporting Information). At last, the photoanode layer was treated with TiCl<sub>4</sub>-H<sub>2</sub>O again. The photoanode was immersed in 0.3 mM N719 dye-ethanol solution for 24 h. For the C101 dye-based DSSC, the photoanode was immersed into a solution composed of 0.3 mM cheno-3a,7a-dihydroxy-5b-cholic acid and 0.3 mM C101 dye in

acetonitrile/tert-butanol solution (1:1 by volume) for 24 h. Pt nanoparticle/FTO glass (GreatCell Solar Limited, Australia) was employed as the benchmark for the performance tests of the developed cathodes, which was preactivated at 400 °C for 0.5 h in air before the DSSC performance tests. The electrolyte composed of 0.03 M I<sub>2</sub>, 0.1 M guanidine thiocyanate, 0.5 M 4-tert-butylpyridine, and 0.6 M 1-butyl-3-methylimidazolium iodide in 85% acetonitrile and 15% valeronitrile (volume ratio) was injected into the space between the electrodes by a capillary effect.<sup>30</sup> J-V curves of DSSCs were obtained by an OAI source meter (230-1A) under simulated sunlight illumination by a solar simulator (OAI's Trisol, 300 W Xe arc lamp), which was calibrated by certified silicon solar cells. The electrode area was around 1.00 cm<sup>2</sup>, and the active area of DSSC was  $0.102 \text{ cm}^2$ , which was well controlled by a square-shaped mask (0.32)  $cm \times 0.32$  cm). Symmetrical cells (identical cathode on both sides) were employed to get Tafel curves and electrochemical impedance spectroscopy (EIS) spectra were obtained by a Zennium electrochemical workstation (ZAHNER), and the frequency ranged from 0.1 to 10<sup>5</sup> Hz. The distance between these two identical electrodes was fixed by a tape with a thickness of 30  $\mu$ m (DuPont Surlyn).

2.3. Characterizations. XRD patterns were acquired by a Bruker D8 ADVANCE X-ray diffractometer (Cu K $\alpha$  radiation) within  $2\theta$ range of 20-80°, and the SEM images were obtained by a Zeiss 55VP instrument. TEM and scanning TEM (STEM, bright-field) images were acquired by an FEI Tecnai G2T20 electron microscope. EDX mappings were conducted using an FEI Tecnai G<sup>2</sup> F30 S-TWIN field emission transmission electron microscope. BET specific surface areas of various samples were acquired by a Micromeritics TriStar II instrument. X-ray photoelectron spectra (XPS) were conducted on a Thermo ESCALAB 250 (monochromatic Al K $\alpha$  radiation, 1486.6 eV). Oxygen vacancy amounts and B-site metal oxidation states of the perovskites were investigated by iodometric titration.<sup>31</sup> Typically, accurately 0.1000 g of perovskite powders were dissolved in HCl + H<sub>2</sub>O solution. Several drops of starch solution were added to the solution as the titration indicator. Finally, thiosulfate  $(S_2O_3^{2-})$ solution was slowly titrated into the above-mentioned solution under the protection of a N2 atmosphere until the color of the solution changed from orange to yellow suddenly. The B-site metal valence states and the oxygen vacancy amounts were then calculated by the  $S_2O_3^{2-}$  amount used. More specifically, the calculation methods are shown below.

The oxygen vacancy ( $\delta$ ) can be obtained by iterative eqs 1 and 2.

$$\delta_{1} = 3 - \frac{X_{A} + X_{B}}{2} = 3 - \frac{\left(X_{A} + 2 + \frac{yM_{I}}{k}\right)}{2}$$
(1)

$$\delta_{n+1} = 3 - \frac{X_{\rm A} + X_{\rm B}}{2} = 3 - \frac{\left(X_{\rm A} + 2 + \frac{y(M_n - 16\delta_n)}{k}\right)}{2} \tag{2}$$

where k = m/M, *m* is the oxide mass (g), *M* is the molar mass of the sample (g mol<sup>-1</sup>), *y* is the consumption of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> molar amount (mol), *X*<sub>A</sub> is the average valence of A-site element of oxides, and *X*<sub>B</sub> is the average valence of B-site element of oxides. The initial  $\delta_0 = 0$  and  $M = M_1$  (the molar mass of oxide when  $\delta_0 = 0$ ).

After iterative calculation, when  $|\delta_{n+1} - \delta_n| < 10^{-5}$ , the final  $\delta$  is the oxygen vacancy amount of the oxides.

Cyclic voltammetry (CV) was conducted in a three-electrode system to test the IRR activity of perovskite/CB composites in acetonitrile containing 0.001 M I<sub>2</sub>, 0.01 M LiI, and 0.1 M LiClO<sub>4</sub> by an electrochemical workstation (CHI760E) at a scan rate of 20 mV s<sup>-1</sup>. Ag/Ag<sup>+</sup> couple and Pt were employed as the reference electrode and CE in the CV test, respectively. Inductively coupled plasma-mass spectroscopy (ICP-MS) was performed on a Varian Vista-Pro instrument. Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) experiment was used to test the surface acidity of the cathodes. The samples were first treated in 20 vol % NH<sub>3</sub>-He at room temperature for 0.5 h and then purged with Ar at 100 °C for 1 h and heated to 500 °C at the rate of 10 °C min<sup>-1</sup>. The NH<sub>3</sub> concentration change during the heating process was detected online by an in situ thermal conductivity detector-based BELCAT-A instrument.

**2.4. Computational Methods.** All calculations were performed with DFT. All model construction, input file generation, and analyses were conducted by using the Python Materials Genomics (pymatgen) materials analysis library<sup>32–34</sup> and the Bader analysis code was provided in Tang et al.'s work.<sup>35</sup> Images of all structural models and electron localization function (ELF) distributions were obtained using the visualization software VESTA.<sup>36</sup>

To investigate I atom adsorption at the LF and Pt surfaces, we implemented the slab model, an interface composed of a vacuum and a slab represented by several atomic layers with the  $a \times b$  plane parallel to a Miller index plane. The slabs were constructed by orienting their corresponding conventional unit cell structure (Figure S8, Supporting Information) such that  $a \times b$  was parallel to the Miller index plane, expanding the oriented unit cell along the c direction and removing several atomic layers as needed to form a vacuum layer.<sup>3</sup> There were two surfaces in each slab and to prevent the divergence of the electrostatic energy, we ensured that both surfaces were symmetrically equivalent. In this study, we investigated the LaFeO<sub>3</sub>(001) and Pt(111) surfaces which were the most energetically stable facets for perovskite and face-centered cubic systems, respectively (Figure S8b-d, Supporting Information). To minimize periodic surface interactions, we used equal slab and vacuum sizes of 15.72 and 13.78 Å for LF and Pt, respectively. Two possible surface terminations were investigated for the LaFeO<sub>3</sub>(001) slabs such as Ferich and La-rich surfaces.

Cl doping was modeled by substituting a single oxygen atom. Figure S8a-c (Supporting Information) shows the possible substitution sites in the bulk and slab systems. For the slab model, Cl was doped at the top surface only. To minimize periodic dopant interactions, we performed Cl-substitution in a  $2 \times 2 \times 1$  bulk supercell for the bulk system and a coverage of 1/4 monolayer (ML) for the slab system. For the Fe-rich surface, Cl was more likely to substitute O at site 0.

The following surface reaction was assumed upon I<sub>2</sub> adsorption

$$\frac{1}{2}I_2 + \text{slab} \rightarrow \frac{I}{\text{slab}}$$
(3)

I atom adsorption under a 1/4 ML coverage was considered in this study. Several possible symmetrically distinct adsorption sites were considered for each slab (Figure S9, Supporting Information). As with Cl-substitution, I atom adsorption was investigated for one surface only (the Cl-doped surface in the case of the Cl-doped slab).

Vienna Ab initio Simulation Package within the projector augmented wave approach was used to perform all DFT energy calculations. <sup>38–40</sup> Strongly correlated electrons were accounted using the Hubbard-*U* corrections for the calculations. Perdew–Berke–Ernzerhof generalized gradient approximation functional was used to model the exchange–correlation effects.<sup>41</sup> All calculations were spin-polarized with a plane wave cutoff energy of 400 eV. The used pseudopotential values were similar to the ones used by the Materials Project.<sup>33,42</sup> The atomic forces and energies of all calculations were converged to within 0.02 eV Å<sup>-1</sup> and 10<sup>-4</sup> eV, respectively. The blocked Davidson iteration scheme and the Methfessel–Paxton method were chosen as the electron minimization and smearing algorithms, respectively,<sup>43,44</sup> and ions were updated using the conjugated gradient algorithm.  $\Gamma$ -Centered *k*-point meshes of 50/*a* × 50/*b* × 50/*c* and 50/*a* × 50/*b* × 1 were used for the oriented unit cell and slab cell calculations, respectively, with noninteger values rounded up to the nearest integer.<sup>52,37</sup>

The relative stability of all clean surfaces was determined using the surface energy

$$\gamma_{hkl} = \frac{E_{\text{slab}}^{hkl,\sigma} - E_{\text{bulk}}}{2A_{\text{slab}}} \tag{4}$$

where  $\gamma_{hkl}$  is the surface energy of a facet with Miller index (*hkl*),  $E_{slab}^{hkl\sigma}$  is the total energy of the slab model with termination  $\sigma$ ,  $E_{bulk}$  is the total energy of the bulk system with the same composition,  $A_{slab}$  is the



Figure 1. (a) TEM and high-angle annular dark-field–STEM–EDX mapping images. (b) HR-TEM images. (c) XPS La  $4p_{3/2}$  and Cl  $2p_{3/2}$  spectra of the LFCl-2 sample.

surface area of the slab structure, and the factor of 2 accounts for the two surfaces in the slab model.

The propensity of the adsorbate to stabilize at a surface site was determined by the adsorption energy based on the following equation

$$E_{ads}^{I} = E_{slab+I} - E_{slab} - \frac{1}{2}E_{I_{2}}$$
(5)

where  $E_{\text{slab+I}}$  is the total energy of the I-adsorbed slab and  $E_{\text{I}_2}$  is the total energy of per atom in an I<sub>2</sub> molecule. The adsorbed slab with the lowest  $E_{\text{ads}}^{\text{I}}$  for each slab was determined to be the most favorable configuration for I<sup>-</sup> adsorption on that surface. For the Cl-doped surfaces, only the most stable configuration for Cl-doping in each termination was considered.

# 3. RESULTS AND DISCUSSION

**3.1. Synthesis and Characterization of the Perovskite-Based Cathodes.** The chlorine-doped LF perovskite oxychlorides were prepared through a complexing technique with  $La(NO_3)_3 \cdot 6H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$  as the cation sources and  $LaCl_3 \cdot 7H_2O$  as both the cation and chlorine source. The doping amount of chlorine in the targeted perovskite materials was tailored by the ratio of  $LaCl_3 \cdot 7H_2O$  to  $La(NO_3)_3 \cdot 6H_2O$  applied in the raw materials during the synthesis. Both EDTA and CA were used as complexing agents to allow the homogeneous distribution of  $La^{3+}$  and  $Fe^{3+}$  in the solution and help the survival of such homogeneity into the gel after the evaporation of water by heating, thus allowing the formation of perovskite phases at relatively low calcination temperature to suppress the loss of chlorine element from evaporation. To confirm the capability of chlorine doping into the oxide site and to determine the solubility of chlorine in the perovskite oxide lattice, three different ratios of LaCl<sub>3</sub>·7H<sub>2</sub>O to La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 0.017, 0.034, and 0.052, were tried for the synthesis of chlorine-doped perovskites. The as-synthesized samples from calcinations of their precursors at 800 °C in the air for 5 h are named as LF, LFCl-1, LFCl-2, and LFCl-3. From the room-temperature XRD patterns (Figure S10, Supporting Information), all XRD peaks for the chlorine-free LF sample can be well indexed as an orthorhombic structure without any impurity. Lattice parameters of 5.565, 7.853, and 5.555 Å (a, b, and c, respectively) were derived from the Rietveld refinement of XRD patterns, which match well with those reported in the literature for the LF perovskite.45 It suggests that the perovskite-type LaFeO3 phase was successfully synthesized. For all three chlorine-doped samples, the main diffraction peaks of LF-like perovskite phase were observed. However, the corresponding peaks slightly shifted to lower angles as compared with that of the undoped LF, suggesting a lattice expansion after the chlorine doping, agreeing well with the larger anion size of Cl<sup>-</sup> (1.81 Å) than  $O^{2-}$  (1.40 Å). It thus provides an indirect support for the successful doping of Clinto the  $O^{2-}$  site in the LaFeO<sub>3</sub> perovskite oxide lattice. On the basis of the XRD Rietveld refinement results (Figure S11 and Table S1, Supporting Information), an impurity phase (LaOCl) started to appear in the LFCl-3 sample, while LF, LFCl-1, and LFCl-2 displayed a pure-phase orthorhombic perovskite structure. It suggests that the chlorine doping amount in LFCl-3 exceeded the solution limit of chlorine in LF.



**Figure 2.** (a) J-V curves of DSSCs with LF, LFCl-1, LFCl-2, LFCl-3, and Pt cathodes, N719 dye, and P25–TiO<sub>2</sub> photoanode under simulated sunlight illumination. (b) J-V curves of DSSCs with Pt and LFCl-2-BM cathodes, TiO<sub>2</sub> microsphere photoanode, and C101 dye tested in both forward and reverse directions. (c) IPCE spectra of DSSCs with Pt and LFCl-2-BM cathodes, C101 dye, and TiO<sub>2</sub> microsphere photoanode. (d) Performance comparison with highly efficient non-Pt cathodes for I<sub>3</sub><sup>-</sup>/I<sup>-</sup>-based DSSCs reported in the literature.

The successful chlorine doping into the LF lattice was also investigated by the high-resolution (HR)-TEM images, STEM with corresponding EDX mapping, and XPS, as shown in Figure 1. From the TEM image in Figure 1a, the LFCl-2 sample showed a particle size of 300-400 nm. A lattice plane distance of 0.278 nm was found in Figure 1b, corresponding to the (121) diffraction plane of the orthorhombic structured perovskite, matching well with the XRD results. The XPS spectrum of LFCl-2 in Figure 1c demonstrated a peak at a binding energy of  $\approx$ 198.5 eV, which corresponded to Cl<sup>-</sup> at Cl 2p<sub>3/2</sub>, suggesting the presence of Cl<sup>-</sup>. La, Fe, O, and Cl elements were detected inside the LFCl-2 nanoparticles based on the STEM-EDX results, further confirming the presence of Cl<sup>-</sup>. The homogeneous elemental distribution of LFCl-2 nanoparticles strongly confirms the successful chlorine doping into the perovskite oxide lattice rather than the formation of an impurity phase. The amounts of chlorine in Cl-doped LF perovskites were then determined by XPS, and the elemental compositions of these Cl-doped LF perovskites can be written as LaFeO<sub>2.977- $\delta$ </sub>Cl<sub>0.023</sub> (LFCl-1), LaFeO<sub>2.965- $\delta$ </sub>Cl<sub>0.035</sub> (LFCl-2), and LaFeO<sub>2.949- $\delta$ </sub>Cl<sub>0.051</sub> (LFCl-3). It should be mentioned that most of the chlorine in the raw materials during the synthesis was lost due to the vaporization, and only a small amount of chlorine was successfully incorporated into the perovskite lattice because of the solubility limit.<sup>46</sup> For instance, partial chlorine was segregated as the LaOCl phase, in addition to the doping into the perovskite lattice for LFCl-3.

**3.2. IRR Activity and DSSC Performance Measurements.** The performance of the as-prepared chlorine-doped LF for catalyzing IRR was first investigated by current density– voltage (J-V) measurements over DSSCs, with LFCl-1, LFCl-2, and LFCl-3 as the cathodes. For comparison, the chlorinefree pristine LF was also evaluated as the cathode in the same way. The chlorine doping into the perovskite structure enhanced the IRR activity of LF effectively, and the PCE of a P25–TiO<sub>2</sub>-based DSSC increased from 3.10% for the LF cathode to 5.55% for the LFCl-1 cathode (Figure 2a and Table S2, Supporting Information). More importantly, the DSSC with the LFCl-2 cathode displayed the highest PCE of 8.20%, surpassing the level of the Pt cathode (7.11%), promising LFCl-2 as a highly efficient cathode for DSSCs. With the further increase in the Cl doping amount, the PCE of DSSC with the LFCl-3 cathode (6.36%) was much lower than that of LFCl-2, which may result from the impurity phase formation in LFCl-3 because of the excessive chlorine doping. The enhanced IRR activity of the LFCl-2 cathode than the pristine LF, Pt, and other Cl-doped LF perovskites was also proved by the charge-transfer resistance  $(R_{ct})$ , as determined by the EIS spectra based on a symmetrical cell configuration (Figure S12, Supporting Information). A low  $R_{ct}$  value suggests a fast charge transport at the cathode/electrolyte interface. On the basis of the equivalent circuit and the EIS fitting values in the inset of Figure S12 and Table S3 (Supporting Information), the calculated R<sub>ct</sub> values of LF, LFCl-1, LFCl-2, LFCl-3, and Pt cathodes are 1.43, 1.09, 0.75, 0.95, and 0.88  $\Omega$   $cm^2,$ respectively. In the Tafel curves, the extrapolated intercept of the cathodic area means the exchange current density  $(I_0)$  and the slope of the extrapolated line is the combination of  $R_{ct}$  and  $R_{\rm s}$ . As can be seen, LFCl-2 displayed the lowest slope and LF showed the highest slope value. Because of the similar  $R_s$  of all five CEs, LFCl-2 presented the best charge-transfer capability among the five CEs based on the Tafel curves (Figure S13, Supporting Information). In addition, a large  $J_0$  means a low  $R_{\rm ct}$  value and a superior electroactivity. LFCl-2 showed the largest  $J_0$  value, corresponding to the lowest  $R_{ct}$  value, agreeing well with the EIS results. It suggests that the IRR performance of these five CEs follow the sequence of LFCl-2 > Pt > LFCl-3 > LFCl-1 > LF, which is in good accordance with the DSSC results, as shown in Figure 2a. It is found that there are some differences in the  $V_{\rm oc}$  of DSSCs with the perovskite and Pt cathodes, which may be attributed to the differences in the thicknesses of perovskite and Pt cathodes. The thickness of the Pt film was around 400 nm (Figure S14, Supporting Information), which was much less than that of the



Figure 3. (a) Oxygen vacancy amounts and the average Fe valence states of LF, LFCl-1, LFCl-2, and LFCl-3 based on oxygen non-stoichiometric results. (b) O 1s and (c) Fe 2p of XPS spectra of LF, LFCl-1, and LFCl-2. (d) ELF distributions of  $LaFeO_3(001)$  with the (1) Fe-rich surface and (2) La-rich surface and of Cl-doped LaFeO\_3(001) with the (3) Fe-rich surface and (4) La-rich surface.

perovskite-based cathode (30  $\mu$ m). The larger thickness of the perovskite-based CE makes the bulk electrolyte layer thinner, which may contribute to the differences in  $V_{\rm oc}$  of DSSCs.<sup>47</sup>

TiO<sub>2</sub> microsphere of larger BET surface area (150 m<sup>2</sup> g<sup>-1</sup>) was used to replace the commercial P25-TiO<sub>2</sub> photoanode (60 m<sup>2</sup> g<sup>-1</sup>) to enhance the PCE of DSSCs by improving the dye adsorption and sunlight harvesting.<sup>30</sup> Furthermore, MWCNTs were also used to replace CB to enhance the dispersity of the perovskite material. DSSC with LFCl-2 cathode and TiO<sub>2</sub> microsphere photoanode displayed a superior PCE of 9.65%, as compared with 8.80% for DSSC with the Pt cathode (Figure S15 and Table S4, Supporting Information). The IRR activity of LFCl-2 was further enhanced through ball milling (denoted as LFCl-2-BM). A much higher PCE of 10.8% was achieved by DSSC with the LFCl-2-BM cathode, suggesting that the particle size also played a critical role in determining the IRR performance of the perovskite cathode, since LFCl-2-BM showed similar elemental composition and oxygen vacancy concentration (LaFeO<sub>2.97- $\delta$ </sub>Cl<sub>0.03</sub> and 0.070) as compared with LFCl-2, which will be discussed later. A very attractive PCE enhancement factor of 23% was obtained by the LFCl-2-BM cathode as compared with Pt. Furthermore, the performance of DSSC with the LFCl-2-BM cathode can be further enhanced by using a more efficient Ru(II)-based C101 dye (Figure 2b and Table S5, Supporting Information). C101 dye was more efficient than the N719 dye in terms of photocurrent density because of the enhanced sunlight harvesting capability.<sup>48</sup> As shown in Figure 2b, the DSSC with the LFCl-2-BM cathode showed PCEs of 11.4 and 11.3% for the forward direction scan and reverse direction scan, respectively. Under the same condition, the DSSC with the Pt cathode displayed PCEs of 9.28 and 9.22% for the forward direction scan and reverse direction scan, respectively, as shown in Figure 2b. LFCl-2-BM cathode displayed much higher PCEs compared to Pt with an improvement factor of 23%. Based on the IPCE spectra of DSSCs with LFCl-2-BM and Pt cathodes in Figure 2c, the

integrated short-circuit photocurrent density ( $J_{sc}$ ) calculated from the IPCE spectra for LFCl-2-BM and Pt cathodes are 19.5 and 19.2 mA cm<sup>-2</sup>, which were only 2.0 and 2.6% lower than the values in the J-V curves, suggesting that the  $J_{sc}$  values in Figure 2b should be reliable. On the basis of the maximum power point tracking of DSSCs with LFCl-2-BM and Pt cathodes in Figure S16 (Supporting Information), DSSC with the Pt cathode presents a stabilized photocurrent density of 16.7 mA cm<sup>-2</sup> at a maximum power output point (voltage = 0.55 V), yielding a stabilized power output of 9.19%, while DSSC with the LFCl-2-BM cathode displays a stabilized photocurrent density of 19.2 mA cm<sup>-2</sup> at a maximum power output point (voltage = 0.59 V), yielding a stabilized power output of 11.3%.

Shown in Figure 2d are the PCEs of non-Pt cathodes and the relevant PCE enhancement factor as compared with the Pt cathode.<sup>4,6-9,12,13,15,49-59</sup> LFCl-2-BM cathode in this work demonstrated much superior PCE and PCE enhancement factor compared to most of the reported non-Pt cathodes. Among the reported highly active non-Pt cathodes, only edgeoriented WS<sub>2</sub> cathode displayed a similar PCE enhancement factor as compared with LFCl-2-BM.<sup>49</sup> However, the absolute PCE value of DSSC with the edge-oriented WS<sub>2</sub> cathode was much lower than that of LFCl-2-BM in this study.<sup>49</sup> We have also investigated the PCEs of DSSCs with pure LFCl-2, CB, and MWCNTs as the cathode, with results depicted in Figure S17 and Table S6 (Supporting Information). It was found that DSSCs with pure LFCl-2, CB, and MWCNTs displayed PCEs of 0.39, 2.33, and 3.71%, respectively. The PCEs of CB and MWCNTs-based DSSCs were similar to the reported PCE values (2.20% for CB and 2.69% for MWCNTs).<sup>60,61</sup> It indicated that the commercial CB and MWCNTs with no modification are not highly active IRR electrocatalysts. The coupling of perovskite and carbon remarkably improved the IRR performance when compared with perovskite or carbon used alone because perovskite contributed active centers and

carbon provided conducting pathways, as reported in our previous work.  $^{3,62}$ 

The enhanced IRR activity of Cl-doped LF was further confirmed by CV, as displayed in Figure S18 (Supporting Information). Two redox couples were observed, which were assigned to two reduction reactions  $(3I_2 + 2e^- = 2I_3^- \text{ and } I_3^- +$  $2e^{-} = 3I^{-}$ ) and two oxidation reactions  $(2I_{3}^{-} - 2e^{-} = 3I_{2}^{-})$  and  $3I^{-} - 2e^{-} = I_{3}^{-}$ ). The positive peaks in CV curves were assigned to the oxidation reactions and the negative peaks corresponded to the reduction reactions. The two peaks in the left part of the CV curves are the major concerns in this work because the DSSC cathodes are accountable for catalyzing the IRR. A higher cathodic peak current density  $(J_{cp})$  and a smaller peak-to-peak separation  $(E_{pp})$  of oxidation/reduction peaks mean a better IRR activity. The  $J_{cp}$  of a CE correlated with the electroactivity of the CE directly, while a smaller  $E_{pp}$  reveals a lower overpotential to trigger the electrocatalytic reaction and a better charge-transfer capability of the cathode.<sup>6-8</sup> The Cl doping effectively decreased the  $E_{pp}$  value and increased the  $J_{cp}$ value of the pristine LF. As shown in Figure S19a (Supporting Information), LFCl-2 displayed a smaller  $E_{pp}$  value (390 mV) than LFCl-1 and LFCl-3 (540 and 490 mV), agreeing well with the sequence in DSSC performance. More importantly, the  $E_{\rm pp}$ value of LFCl-2 was much smaller than that of Pt (480 mV) further confirming LFCl-2 as a superior electrocatalyst for IRR. It was observed that  $J_{cp}$  of the LFCl-2 cathode was higher than those of LF, LFCl-1, LFCl-3, and Pt cathodes, indicating a much higher electrocatalytic activity of LFCl-2 for IRR (Figure S19b, Supporting Information), which will be discussed in the following section.

3.3. Factors To Determine the IRR Activity of Perovskite-Based Cathodes. It is well known that the oxygen vacancies and the  $\sigma^*$ -orbital (e<sub>g</sub>) occupation state greatly affect the OER/ORR activity of perovskite oxide in an alkaline electrolyte.<sup>23,24</sup> It was also pointed out the introduction of oxygen vacancies into oxides greatly increased the activity for IRR.<sup>17</sup> The oxygen vacancy amounts of pristine LF and the various chlorine-doped LF were then studied by an iodometric titration method. The oxidation state of iron was +3 in the pristine LF perovskite, suggesting its zero oxygen nonstoichiometry. By doping Cl<sup>-</sup> into the perovskite lattice of LF, a reduction in the average Fe valence state was observed while the average valence states of iron in LFCl-1, LFCl-2, and LFCl-3 were 2.92, 2.82, and 2.79, respectively, as shown in Figure 3a. Correspondingly, the oxygen vacancy concentrations in LFCl-1, LFCl-2, and LFCl-3 were 0.029, 0.073, and 0.079, respectively. Such a trend in oxygen vacancy concentration agrees well with a previous report on Cldoped perovskites.<sup>63</sup> The increased oxygen vacancy concentration from chlorine doping likely accounts for the outstanding performance of LFCl-2 as a DSSC cathode.

The increased oxygen vacancy concentration in the LF perovskite after the chlorine doping was further confirmed by the XPS characterization. On the basis of the O 1s XPS spectra of LF, LFCl-1, and LFCl-2 in Figure 3b, the amount of lattice oxygen in LF reduced dramatically from 47.0 to 38.0 and 29.8% in LFCl-1 and LFCl-2, respectively (Table S7, Supporting Information). The reduction in the amount of the lattice oxygen in LF is due to the creation of oxygen vacancies by Cl doping. It is reported that the occupancy of the lattice oxygen amount.<sup>31</sup> That is to say, the increased oxygen vacancy caused by Cl doping in this study can decrease the

lattice oxygen amount in the perovskite oxides. Furthermore, it suggested that LFCl-2 displayed more oxygen vacancies than LFCl-1, which is in good accordance with the oxygen vacancy results. In addition, the formation of the highly oxidative oxygen species  $(O_2^{2-}/O_1^{-})$  was related to the creation of surface oxygen vacancies.<sup>64</sup> The much higher amount of  $O_2^{2-}/$ O<sup>-</sup> species in LFCl-2 than in LF and LFCl-1 further confirmed the higher oxygen vacancy concentration in LFCl-2. According to the Fe 2p XPS spectra in Figure 3c, although Fe  $2p_{3/2}$  and  $2p_{1/2}$  binding energies (710.8 and 724.5 eV) were consistent with  $Fe^{3+}$  in the samples, the negative shift of Fe 2p peaks in the LFCl-1 and LFCl-2 suggested the presence of Fe in a lower oxidation state (Fe<sup>2+</sup>). In addition, LFCl-2 displayed more Fe<sup>2+</sup> species as compared with LFCl-1 (17.08 vs 7.94 mol %). All of the above results strongly suggested that the different IRR activities of LFCl-1 and LFCl-2 were closely related to the different oxygen vacancy concentrations. Although LFCl-3 presented an oxygen vacancy similar to that of LFCl-2, the LaOCl impurity in LFCl-3 led to lower IRR activity. We prepared the pure LaOCl by heating LaCl<sub>3</sub>·7H<sub>2</sub>O at 450 °C for 2 h. As displayed in Figure S20a,b (Supporting Information), the XRD pattern suggested that a pure LaOCl phase was obtained, and DSSC with LaOCl/CB (1:1) CE displayed a very low PCE of 1.71%, which was even lower than that of pure CB (2.23%) and much lower than those of LFCl-2 and LFCl-3 (8.20 and 6.36%), suggesting the inactive nature of LaOCl for IRR. Thus, the lower IRR activity of LFCl-3 than LFCl-2 is likely attributed to the lower IRR activity of the LaOCl impurity in LFCl-3.

It is surprising that the Cl doping decreased the Fe valence state in LF because a recent study demonstrated that the average B-site metal valence increased and the oxygen vacancy concentration decreased after doping of F<sup>-</sup> into SrFeO<sub>3- $\delta$ </sub> and SrFe<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3- $\delta$ </sub>.<sup>31</sup> Upon the doping of an anion with a higher valence state, like F<sup>-</sup> into the O<sup>2-</sup> site, in order to keep charge neutrality, a reduction in the Fe valence state or the oxygen vacancy amount could appear. However, because of the larger anion size of Cl<sup>-</sup> (1.81 Å) than O<sup>2-</sup> (1.40 Å), the Cl<sup>-</sup> doping likely promoted the reduction of iron in the B-site of LF to lower oxidation state (i.e., to gain a larger cation size) to release the internal stress in the perovskite oxide lattice. As a result, some oxygen vacancies were formed to keep the electric charge neutrality.

ELF and Bader analysis on La-rich and Fe-rich terminations of the LaFeO<sub>3</sub>(001) surfaces were performed to reveal the valence changes of La and Fe elements after Cl doping based on the charge transfer between the different elements. The difference in the charges for each element ranged from a scale of 0–1. For the Fe-rich surface, the introduction of the Cl dopant reduced the valence of the adjacent Fe atom by approximately 0.26 in Figure 3d. Meanwhile, for the La-rich surface, the introduction of the Cl dopant showed no obvious change in the valence of the adjacent La atom in Figure 3d. The DFT and experimental results matched well with each other, demonstrating that the Cl doping in LF reduced the valence state of the B-site metal.

Besides the oxygen vacancy amounts and the B-site Fe valence states, the IRR activity of an electrocatalyst is also related to the particle size and the BET specific surface area. A reduction in the particle size of the metal oxide-based electrocatalysts provided more active sites for IRR and higher performance in DSSCs.<sup>65</sup> The highest IRR activity of LFCl-2 among the three Cl-doped LF perovskites was also contributed





partially from its smallest particle size and biggest surface area, as estimated from the SEM images and BET measurements (Figures S21 and S22, Supporting Information). In addition, the much improved IRR activity of LFCI-2-BM as compared to LFCI-2 was assigned to the further reduced particle size and an enlarged BET specific surface area (Figure S23, Supporting Information). On the basis of the nitrogen adsorption/desorption isotherms of LFCI-2/MWCNTs and LFCI-2-BM/MWCNTs in Figure S24 (Supporting Information), LFCI-2-BM/MWCNTs also showed a higher BET surface area than LFCI-2/MWCNTs, which may contribute to the higher IRR activity. As displayed in Figure S25 (Supporting Information), LFCI-2-BM displayed a further reduced  $E_{\rm pp}$  value and an increased  $J_{\rm cp}$  value in the CV profile as compared with LFCI-2 (310 mV and -1.12 mA cm<sup>-2</sup> for LFCI-2-BM; 390 mV and -0.867 mA cm<sup>-2</sup> for LFCI-2).

**3.4. IRR Mechanism and Possible Activity Origin of CI-Doped LF Perovskite Cathodes.** On the basis of our experimental results and previous fundamental understanding about the IRR mechanism in the literature,<sup>16,17</sup> here we propose a possible mechanism for IRR on perovskite-based cathodes (eqs 6–9 and Figure 4), where B-site transition metal-containing centers and oxygen vacancies functioned as the active sites for IRR. As shown below, the IRR on the perovskite proceeds in three steps.

Overall reaction:  $I_3^{-}(sol) + 2e^{-} \rightarrow 3I^{-}(sol)$  (6)

Step 1: 
$$I_3^{-}(sol) \rightarrow I_2(sol) + I^{-}(sol)$$
 (7)

Step 2: 
$$2M^{n+} + I_2(sol) + 2V_0^{\bullet\bullet} + 2e^- \rightarrow 2M^{(n+1)+} + 2I_0^{\times}$$
(8)

Step 3: 
$$M^{(n+1)+} + I_o^{\times} \rightarrow M^{n+} + I^{-}(sol) + V_O^{\bullet \bullet}$$
 (9)

where  $V_0^{\bullet\bullet}$  is the double charged oxygen vacancy in the perovskite;  $I_0^{\times}$  is the iodine ion in an oxygen site; M means the B-site metal; and sol indicates the acetonitrile-based solution. By using a perovskite as the electrocatalyst for IRR, once the surface B-site metal ions were oxidized or reduced, they can be promptly regenerated by the charge transfer from the bulk to the surface of the perovskite oxide because of the mixed conducting properties of perovskites. The oxygen vacancies of the perovskite oxide also played a crucial role in the adsorption/occupation of I<sub>2</sub> on the perovskite surface as well as the redox processes between  $M^{(n+1)+}$  and  $M^{n+}$ . Therefore, the larger oxygen vacancy amount and the lower B-site metal oxidation state played essential roles to obtain higher IRR performance. As shown in Figure 4, the chlorine doping led to

increased oxygen vacancy concentration and enriched Fe<sup>2+</sup> ions and thus an enhancement of active sites and then the IRR activity. Notably, LFCl-2 exhibited much better IRR activity than another pure-phase Cl-doped perovskite (LFCl-1), which was attributed to the larger amounts of oxygen vacancy and Fe<sup>2+</sup> ions, smaller particle size, and larger BET specific surface area, as discussed earlier.

The possible activity origin of the Cl-doped LF cathode was studied by DFT calculations. The slab cells from the fully relaxed LF were constructed to model the (001) surface and its interaction with dopants and adsorbates. The surface energy and adsorption energy of the slab systems are shown in Table S8 (Supporting Information). The La-rich surface of  $LaFeO_3(001)$  was more stable than the Fe-rich surface by 0.21 J m<sup>-2</sup>. The surface energy of the Pt(111) surface was in good agreement with previous computational results.<sup>32</sup> It was found that the Cl doping in LF promoted the I atom adsorption on the surface, which benefited the IRR process. Among the five different surfaces investigated, the I atom adsorption onto the La-rich surface of Cl-doped  $LaFeO_3(001)$ was significantly more stable than that on the La-rich surface of  $LaFeO_3(001)$  and even the Pt(111) surface. In addition, the I atom adsorption energy in the Cl-doped Fe-rich surface was slightly more stable by 0.02 eV than that in the pristine Fe-rich surface.

For perovskite oxides, two types of terminations along the (001) surface including the BO<sub>2</sub> (B-rich) and AO (A-rich) terminations were obtained. Transition metals such as Pt are known to have excellent catalytic activities because of their involvement in enabling redox reactions. In a perovskite system, these transition metals often take the place of the B cation, creating a BO<sub>2</sub> layer of atoms in the slab which alternates with the AO layers. This BO<sub>2</sub> layer was the original impetus for studying the catalytic effects of LF on the IRR and has been shown in previous ab initio studies to have excellent catalytic activities.<sup>66,67</sup> In addition to the contributions of FeO<sub>2</sub>, our results showed that the Cl atom substitution on the LaO surface significantly promoted the adsorption of I atom because of the relatively inert effect on charge transfer of the Cl atom on the La-rich surface, which led to a better interaction between the La-rich surface and the Cl dopant, as evidenced by the Bader analysis. The synergistic effect of Cl dopants on the La-rich termination of LF and the active FeO<sub>2</sub> layer may contribute to the superior IRR activity of Cl-doped LF, and the IRR activity can be further optimized by tailoring the Cl doping amounts as demonstrated by our experimental results.

**3.5. IRR Stability Test.** Besides the IRR activity, stability is also a crucial parameter that should be taken into serious



**Figure 5.** (a) CV stability tests of LF, LFCl-2, and Pt CEs in the  $I_3^-/I^-$ -based electrolyte. (b) CV profiles of LFCl-2 cathode in CV stability tests. (c) NH<sub>3</sub>-TPD profiles of LF and LFCl-2 samples. (d) J-V curves of DSSCs with LF, LFCl-2 CEs with and without the treatment in the electrolyte for 28 days, N719 dye, and P25–TiO<sub>2</sub> photoanode under simulated sunlight illumination.

consideration in the development of alternative cathodes for DSSCs. As displayed in Figures 5a,b and S26 (Supporting Information), after 40 CV cycles, the  $E_{\rm pp}$  value for the Pt cathode increased from 480 to 980 mV, suggesting poor stability of the Pt cathode for IRR. In contrast, LF showed better stability for 100 CV cycles with a slight increase in the  $E_{\rm pp}$  value (570 to 600 mV). LFCl-2 exhibited even much better stability for 100 CV cycles without any obvious increase in the  $E_{\rm pp}$  value. The peak current densities of the LFCl-2 cathode were almost unchanged after 100 cycles, suggesting a superior IRR durability (Figure S27, Supporting Information).

The structural stability of LF and LFCl-2 was further comparatively studied by treating the powder in the electrolyte for 28 days. Both LFCl-2 and LF still displayed a pure perovskite phase after the treatment of the liquid electrolyte (Figure S28 and Table S9, Supporting Information). However, according to the ICP-MS results, La and Fe element leaching (155 and 362 mg  $L^{-1}$ , respectively) was observed in the electrolyte solution that was used for the treatment of LF, whereas no such metal leaching (less than  $1 \text{ mg } L^{-1}$ ) appeared for LFCl-2. This demonstrated that chlorine doping improved the structural stability of LF perovskite in the electrolyte. The estimated molar percentages of La and Fe leached from the LF perovskite after the treatment were 0.683 and 3.95 mol %, respectively. The much higher degree of Fe leaching than La leaching can be assigned to the much higher La-I bond energy than that of Fe–I (411 vs 123 kJ mol<sup>-1</sup>). The much superior structural stability of LFCl-2 to LF in the electrolyte was assigned to the improved surface acidity by Cl doping, as supported by NH<sub>3</sub>-TPD results in Figure 5c. The effect of the structural stability of LF and LFCl-2 cathodes on the DSSC performance was also conducted. The PCE of DSSC with treated LFCl-2 CE maintained 99% as compared with the asprepared LFCl-2 (8.14 vs 8.20%), as displayed in Figure 5d and Table S10 (Supporting Information). Nonetheless, the PCE of treated LF-based DSSCs reduced to 58% as compared with as-prepared LF (1.81 vs 3.10%) because of the perovskite

phase loss and the enriched  $La_2O_3$  phase on the surface, suggesting that chlorine doping played an important role in the achievement of high stability by reducing the metal element leaching behavior of the perovskite-based cathodes.

## 4. CONCLUSIONS

In conclusion, Cl-doped LF perovskite oxychlorides synthesized by a simple sol-gel route were demonstrated as new, highly active, stable and cost-effective cathodes in DSSCs. The Cl doping remarkably improved the IRR activity of nondoped parent LF because of the creation of oxygen vacancies and lower B-site metal oxidation states, as evidenced by both experimental results and DFT calculations. The PCE achieved using this new LFCl-2 cathode was 11.4% as compared with the Pt cathode (9.28%) when TiO<sub>2</sub> microsphere was used as an advanced photoanode for C101 dye-based DSSCs, which was higher than most of the reported high-performance non-Pt cathodes in  $I_3^{-}/I^{-}$  electrolyte-based DSSCs. Furthermore, LFCl-2 cathode showed enhanced IRR stability as compared with LF because of the improved surface acidity as introduced by Cl doping. These results suggest that Cl-doped LF perovskite is an efficient and cost-effective DSSC cathode to substitute Pt and presents a new way to enhance the activity and stability of electrocatalysts for IRR in the  $I_3^{-}/I^{-}$  redox couple-mediated photoelectrochemical and electrochemical devices such as photoassisted lithium-oxygen batteries and rechargeable lithium-iodine batteries.68,69

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b07966.

Physical properties and (photo)electrochemical investigations of perovskite-based CEs,  $TiO_2$  microsphere, and P25–TiO<sub>2</sub> photoanode, theoretical calculation results, and solar cell performance tests (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: zongping.shao@curtin.edu.au.

# ORCID 6

Chi Chen: 0000-0001-8008-7043

Shyue Ping Ong: 0000-0001-5726-2587 Lianzhou Wang: 0000-0002-5947-306X Wei Zhou: 0000-0003-0322-095X

Zongping Shao: 0000-0002-4538-4218

### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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#### Notes

The authors declare no competing financial interest.

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