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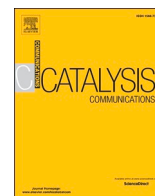
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Well performing Fe-SnO₂ for CO₂ reduction to HCOOH

U. Savino^{a,b,*}, A. Sacco^a, K. Bejtka^{a,b}, M. Castellino^b, M.A. Farkhondehfal^a, A. Chiodoni^a, F. Pirri^{a,b}, E. Tresso^b

^a Center for Sustainable Future Technologies @ POLITO, Istituto Italiano di Tecnologia, Via Livorno 60, 10144 Turin, Italy

^b Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy

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ABSTRACT

The climate change imposes to mankind a severe management of CO₂ emissions in atmosphere. CO₂ valorization through electrocatalysis revealed to be a valuable solution to this global issue. SnO₂ is an electrocatalyst widely investigated for its capability to reduce CO₂ to formic acid. In particular, mesoporous SnO₂ offers a high adsorption capability, resulting in a high catalytic activity. In order to improve its performance, Fe-doping is here investigated for the first time. We observed that Fe-doped SnO₂ exhibits a remarkable 100% enhancement of the partial current density for HCOOH production at relatively low overpotentials, although keeping the selectivity unchanged.

1. Introduction

According to the Paris agreement, the control of climate change imposes a common effort among all the nations through the control and limitation of CO₂ emissions in atmosphere. In order to reach this goal, different strategies have been adopted. [1–3] Among them, catalytic CO₂ reduction reaction (CO₂RR) is the more valuable since it allows to convert CO₂ into a resource, namely a carbon-based fuel or a chemical.

Aiming to obtain a novel, well-performing, cheap and easily scalable catalyst, the attention has been focused on tin oxide (SnO₂) and its doped forms. Tin oxide is an attractive semiconductive material with high catalytic power and non-noble, eco-friendly and low-cost characteristics. [4] From the catalytic point of view, SnO₂ is particularly interesting because of its high selectivity to formic acid (HCOOH). [5] From the perspective of a large-scale application of the catalyst, the selectivity would ease the CO₂RR product separation: the liquid HCOOH from the gaseous minor products (CO and H₂).

A great number of methods have been developed until now to prepare nanostructured SnO₂ catalysts [6–8] Among them, anodic-oxidation (AO) of tin foils unveiled to be a simple, high yield, low-cost, scalable, easily reproducible and effective strategy to prepare nanostructured porous materials. [9] As already demonstrated by Bejtka et al., [10] sponge-like SnO₂ realized via AO is capable to reduce CO₂ to formic acid with good selectivity.

The main chasing properties of a performing electrocatalyst are (i)

the good selectivity through products, (ii) the low energy requirements, i.e. the lower the reaction over-potential the better, and (iii) the high electron transfer, which stands for high current densities at low bias. The applied potential for SnO₂-based catalysts is commonly more negative than –1 V vs Reversible Hydrogen Electrode (RHE). Only few works are reported in literature with a lower overpotential (around –0.8 V vs RHE). As an example, Kumar et al. [7] realized SnO₂ nanoparticles capable to reduce CO₂ to HCOOH at –0.8 V vs RHE, although with a partial current of just –1.4 mA/cm². A similar result was obtained by the same group with porous nanowalls, [7] and by Ge et al. [11] with mesoporous structures. In order to reach higher partial currents, the potential has to be more negative. Partial current densities over –10 mA/cm² were reached with Sn dendrite [12] and chainlike mesoporous SnO₂, [10] but with applied potentials lower than –1.1 V vs RHE.

To overcome these limitations, doping has been investigated [13,14] as a possible way to induce nanostructure modification, together with the density of states engineering to push the catalytic properties of SnO₂ toward CO₂ reduction at lower overpotentials.

As proved by literature, in systems containing metals, like Au and Cu, the broken spatial symmetry near grain boundaries changes the binding energy of the reaction intermediates, facilitating the CO₂ reduction to CO [15] and its reduction to C₂₊ products, [16] thus arousing the attention in the study of modified-SnO₂. The effect of doping results in an upward shift in the Pourbaix diagram boundary separating the [3H/1CO₂] and [4H/1CO₂] states. This means that dopants should lower the

* Corresponding author at: Center for Sustainable Future Technologies @ POLITO, Istituto Italiano di Tecnologia, Via Livorno 60, 10144 Turin, Italy.

E-mail address: umbe.sav@gmail.com (U. Savino).

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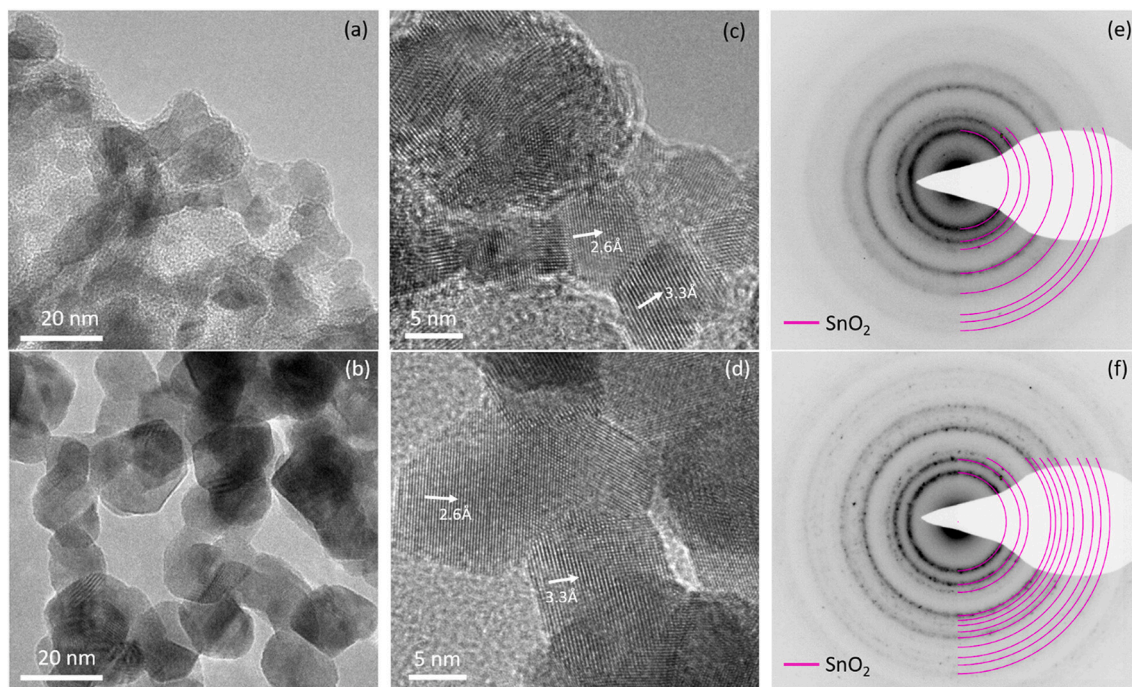


Fig. 1. TEM characterization: BF-TEM (a, b) HR-TEM (c, d) and SAED (e, f) for SnO₂ (a, c, e) and Fe-SnO₂ (b, d, f) respectively. In HR-TEM images interplanar spacings calculated from FFT (not shown) are provided (~ 3.3 Å (110), ~ 2.6 Å (101) family of planes of the SnO₂ structure). In SAED images a simulated pattern for SnO₂ crystal structure is also shown.

over-potential for CO₂ reduction with respect to un-doped tin oxide. For this reason, doping has been suggested by Saravanan et al. [14] as good strategy for future experimental investigations on energetically efficient CO₂ reduction.

We selected Fe-doping because the inclusion of Fe³⁺ ion is expected to induce a p-type behaviour in SnO₂, thus increasing the resistivity of the material [20–22], and to introduce oxygen vacancies [22,23] which are beneficial for CO₂RR. Albeit Fe-doped SnO₂ has been already investigated for different applications, [17–23] to the best of our knowledge it has never been studied as electrocatalyst for CO₂RR.

SnO₂ was synthesized via AO, following the procedure presented by Bejtka et al. [10]. The doping has been attained following the procedure developed by Jain et al. [24] on Ni-doped SnO₂ (synthesis reported in the SI). The same dopant molar concentration and synthesis parameters were kept in order to establish a starting procedure. A complete structural characterization has been carried on. Fe-doped SnO₂ has been then tested as electrocatalyst for CO₂RR. As a result, the material exhibits a good selectivity toward formic acid (HCOOH) with a secondary production of CO and H₂. The selectivity toward HCOOH and CO is taken as a great advantage since they are easily separable; moreover, CO and H₂ can be employed to obtain syngas. [25]

2. Results and discussion

2.1. Material characterization

The un-doped SnO₂ samples annealed at 600 °C display a porous and irregular structure (Fig. S1 a–b), composed by nanochannels, with about 50 nm mean diameter and wall thickness of about 15 nm, which is typical for SnO₂ prepared by anodic oxidation. [10] The TEM characterization shown in Fig. 1 a and c gives more detailed information on morphological and structural properties. The bright field (BF) and HR-TEM show that the pore walls are made of small-interconnected crystals, with a size in the range of 5–20 nm. The ring pattern in Selected Area Electron Diffraction (SAED), analyzed with the Circular Hough analysis tool [26] of Digital Micrograph™ software, confirms the

polycrystalline nature of the sample, and the crystalline phase present of SnO₂ (tin oxide, JCPDS 00–041-1445).

The mesoporous structure, created during the synthetic process, allow the easy access of the electrolyte to the catalytic sites and efficient mass diffusion. [11] Moreover, the nanostructuring with tailored surface configuration proved to be an effective strategy to enhance the catalytic activity. [15,16]

Vertically aligned nanochannels were observed in SnO₂ realized by anodic oxidation by the group of Palacios-Padròs [27] and in our previous work, [10] with fully open pores, whose diameter is compatible with the one we measured. This implies that the increase of the annealing temperature to 600 °C (necessary for the doping step) does not affect the sample morphology.

The introduction of Fe into SnO₂ sample leads to the formation of bigger crystals, with good crystallinity (Fig. 1e), clearly discernible in the FESEM (Fig. S1 c) and BF-TEM (Fig. 1d) images. The increased crystal-size, which, on the basis of HR-TEM images, is of about 12–35 nm, causes the closure of the channels, which are no more discernible in the top-view FESEM image (Fig. S1 c). The structural characterization by SAED shows the ring pattern with reflections from numerous SnO₂ planes (tin oxide, JCPDS 00–041-1445), with no significant distortion to the unit cell. Although there is no detectable evidence of the dopant in the diffraction pattern, the EDX analysis confirms the presence of Fe in the doped-SnO₂ powder samples, as shown in Fig. S2. The lack of any evidence of the presence of metal clusters neither in HR-TEM nor in SAED suggests the dopants are well spread and completely inserted in the SnO₂ lattice.

A further investigation of the crystalline structure of the SnO₂ samples was carried out with XRD in Bragg-Brentano configuration. The obtained patterns correspond to SnO₂ (JCPDS 00–041-1445) with no significant variations of peak positions among the doped and un-doped samples (Fig. S3). The peak shape and FWHM in the un-doped sample give evidence of small coherent diffraction domains in this sample. Narrower peaks observed in Fe-SnO₂, which according to the Scherrer equation, give the evidence of increased size of coherent diffraction domains with respect to the un-doped sample, and this is consistent with

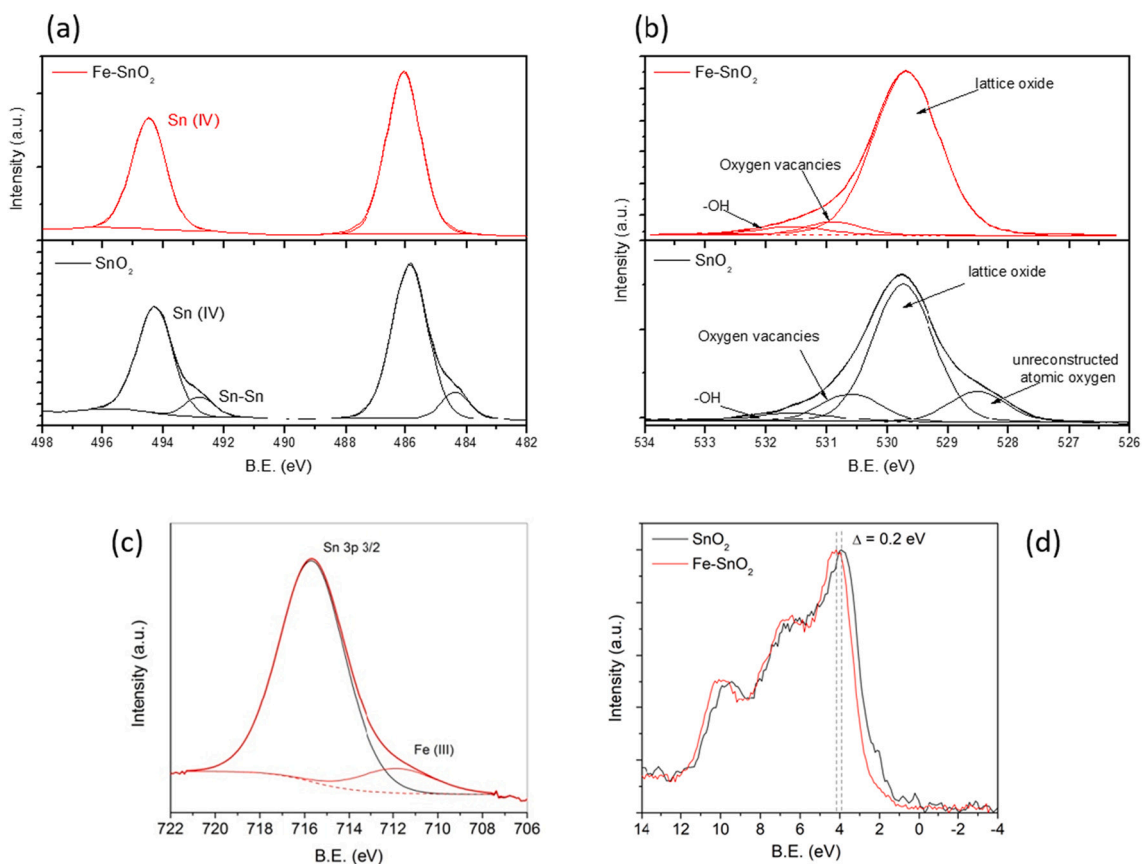


Fig. 2. XPS spectra of Sn 3d and O 1s orbitals of SnO₂ (a) and Fe-SnO₂ (b) respectively. Fe 2p of Fe-SnO₂ sample (c) and valence band spectra (d) are also shown. For sake of clarity, the spectra referred to SnO₂ are black, while the ones related to Fe-SnO₂ are red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the TEM observation. The result is also in good agreement with the outcomes of Kaur et al. who found that Fe incorporation in SnO₂ lattice resulted in increasing grains size. [28]

Concerning the surface chemical composition, SnO₂ samples were characterized with XPS, using C 1s peak (284.5 eV) to calibrate the spectra.

The survey spectra are reported in Fig. S4; Sn and O were observed in both samples, with small traces of adventitious carbon. Fe has been observed in the Fe-SnO₂ samples, which is consistent with the EDX results.

The Sn 3d doublet of SnO₂ sample is located at 485.9 eV (Sn 3d_{5/2}) and 494.3 eV (Sn 3d_{3/2}) as shown in Fig. 2 a. Since the peaks due to Sn (II) and Sn (IV) are close to each other, it is not trivial to distinguish the oxidation state of the compound. For this reason, the valence band (VB) shape has been used for the identification: as shown in Fig. 2 d, the VB region displays the typical SnO₂ three-peaked structure. [29] Thus the most abundant oxidation state results to be Sn (IV), as also suggested by the 8.4 eV peaks distance related to the spin-orbit split. [10]

The small shoulders at lower binding energy (484.4 eV and 492.8 eV) can be ascribed to Sn—Sn, as reported by R. Shiratsuchi et al. [30]

The O 1s spectrum (Fig. 2 b) confirms the presence of lattice oxide, displaying a strong component located at 529.7 eV, a small contribution due to O surface vacancies at 530.6 eV and a smaller component due to —OH species, as defined by the component at 531.5 eV. [31] A further peak located at 528.5 eV can be ascribed to unreconstructed atomic Oxygen, as reported by T.E. Jones et al. [32]

As regard Fe-SnO₂, the shift due to Sn—Sn bond in Sn3d doublet (see Fig. 2 a) and the peak due to O1s lowest chemical shift at 528.5 eV (Fig. 2 b) are disappeared. For both samples the presence of the Oxygen vacancy related peak is of fundamental importance since for application

in CO₂ valorisation, oxygen vacancies are believed to participate in the catalysis by enhancing CO₂ adsorption and, as a consequence, its reduction.

As regard the dopant (Fig. 2 c), the peak maximum of Fe 2p_{3/2} stands at 711.7 eV. The position is connected to the oxidation state of Fe (III), [33] thus suggesting that iron was successfully inserted in the oxide structure. The close peak, located at 715.5 eV is referred to Sn 3p_{3/2}, which is partially overlapping the Fe 2p doublet, as also observed by Xing et al. [34]

By looking at the VB region (Fig. 2 d), a 0.2 eV shift at higher binding energies has been observed for Fe-SnO₂. A similar outcome has been already published in literature by Egdell et al. [35] in their study concerning Sb-doped SnO₂ materials. In their findings the experimental results were explained by the presence of segregated doping atoms at the surface, a phenomenon which induces a shrinkage in the energy gap and a subsequent shift toward higher binding energies of the VB onset, thus proving the doping achievement.

2.2. Electrochemical and CO₂ reduction tests

Prior to CO₂RR test, CV has been carried out to first check the performances of the doped and un-doped samples. The CV plot in Fig. S5 shows that with equal potential, Fe-SnO₂ exhibits a higher current than SnO₂, which means that the Fe-doped electrodes have higher activity (higher geometric current).

The doped and un-doped SnO₂ samples have been, then, tested for CO₂RR in the same potential range (from -0.69 to -0.89 V vs RHE), and the production of formic acid has been analyzed.

As a result, the un-doped SnO₂ exhibits a maximum of HCOOH production, 40.0% of Faradaic efficiency (FE, eq. S1), at -0.89 V vs RHE

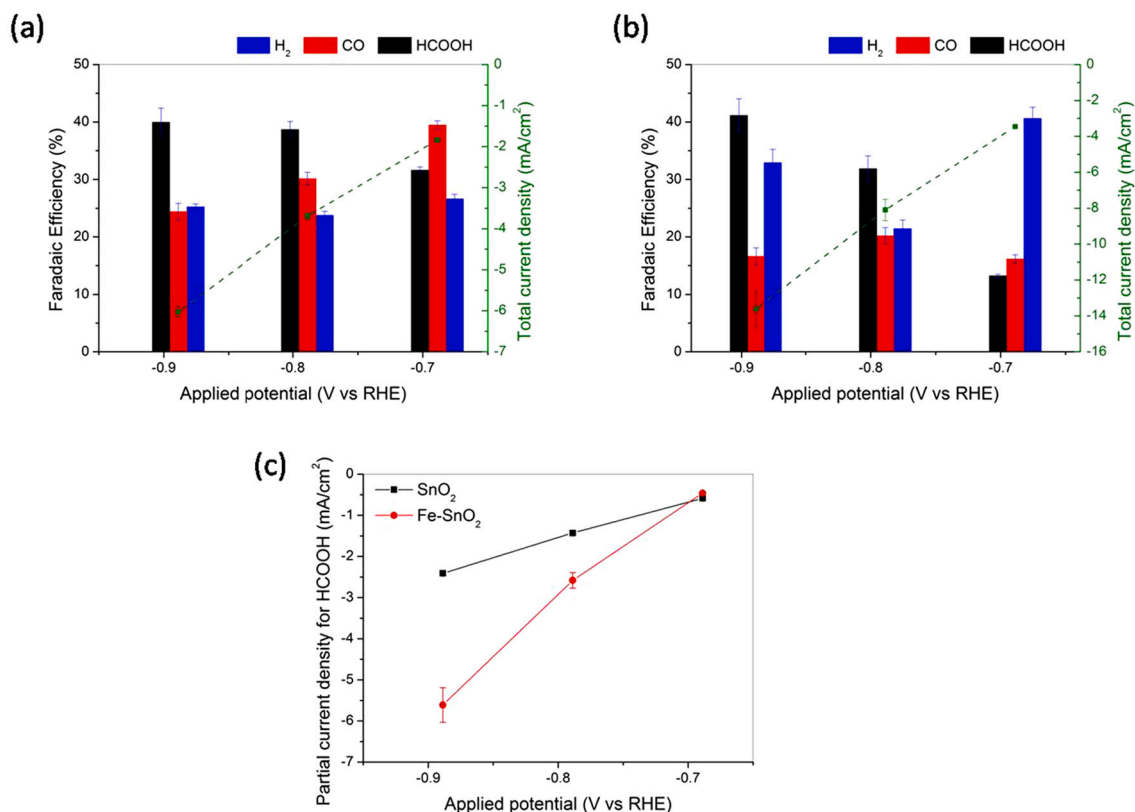


Fig. 3. Bar chart representing the Faradaic efficiencies for SnO₂ (a) and Fe-SnO₂ (b) for each tested potential. In green, the current density curve shows the behaviour at different applied potentials. (c) Partial current densities related to HCOOH production. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

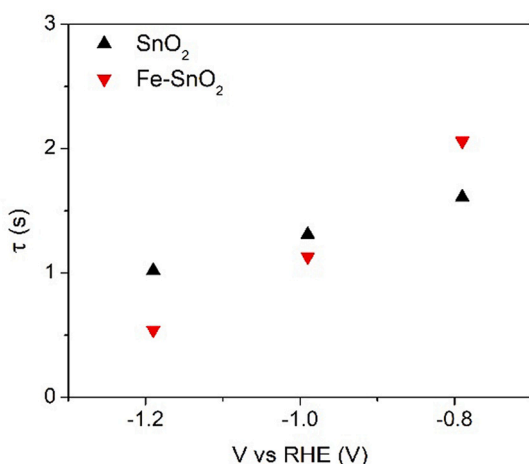


Fig. 4. Charge transfer time calculated for SnO₂ and Fe-SnO₂.

with a secondary production of H₂ and CO (Fig. 3 a). A stable total current density of -6.0 mA/cm^2 is obtained during 1 h of CO₂ reduction as shown in Fig. S6. The resulting FE is compatible to the one reported by Ge et al. [11] on mesoporous SnO₂, albeit with lower current densities. Moreover, the FE for HCOOH production is lower with respect to our previous work on SnO₂ electrocatalyst calcined at 450 °C; [10] however, it is worth notice that the over-potential corresponding to maximum HCOOH production has been lowered in the present work.

Similarly, Fe-SnO₂ exhibits the maximum of HCOOH production at the same potential (-0.89 V vs RHE) with a FE of 41% (Fig. 3 b). At this potential, CO₂ is reduced mainly to HCOOH, with H₂ and CO as

secondary products. It is worth noting that the total current density of Fe-SnO₂ is more than two times higher than SnO₂, with a value at the equilibrium of -14 mA/cm^2 . Thus, keeping the same selectivity of bare SnO₂, it is possible to double the efficiency of CO₂ reduction, as evident from the HCOOH partial current densities calculated through eq. S2 (Fig. 3 c), to easily separable products. As expected, while the applied potential negatively increases, the equilibrium of the reaction moves from CO₂ reduction to H₂ evolution: for this reason, potentials more negative than -0.89 V vs RHE have not been investigated (further discussion on the reaction mechanism in the Supporting Information). The low overpotential makes the sample particularly interesting, especially for its relatively high current. The obtained high activity for HCOOH production (5.44 mA/cm^2) results to be among the highest ever reported for tin-oxide based electrocatalysts at potentials higher than -1 V vs RHE , as reported in Table S1.

The performance of Fe-SnO₂ has been investigated via EIS. By analyzing the impedance of both the samples (Fig. S7), a different behaviour of the charge transfer kinetics has been observed at the catalyst/electrolyte interface. In fact, by looking at the transfer time (Fig. 4), it is possible to observe a faster kinetic for Fe-SnO₂ with respect to bare SnO₂ while the potential is increasing. This implies that, in the former catalyst, a larger number of charges is available at the surface for the reduction reactions.

This result confirms that Fe-doping is an effective strategy in improving the performance of SnO₂ catalyst for CO₂RR.

3. Conclusion

A cheap and easily scalable technique to fabricate Fe-doped SnO₂ has been presented. The material has been tested for the first time for CO₂RR and demonstrated to be a valuable electrocatalyst for HCOOH

production. The highly porous structure, observed with FESEM, offers a high concentration of catalytic centres per unit area. Moreover, the presence of Fe-doping, confirmed by XPS analysis, demonstrated to be capable to keep the same selectivity of SnO₂, but increasing the production rate. In fact, a 100% enhancement of current density was observed at a relatively low potential of -0.89 V. The analysis of the impedance through EIS allowed to explain the result showing a faster charge transfer of Fe-SnO₂ sample with respect to SnO₂. In order to complete the investigation on the catalyst, stability tests will be carried out and the results will be presented in a future broader publication.

Although a further optimization of the catalyst is still possible, nevertheless, Fe-doped SnO₂ demonstrates to be a promising material for future technologies for CO₂RR.

Data availability

The data are available by contacting the corresponding author.

Author contribution and ORCID

Umberto Savino (ORCID: 0000-0003-1884-2444).

Conceptualization and synthesis of the materials. Electrochemical measurements, gas-products measurement, data analysis and interpretation.

Adriano Sacco (ORCID: 0000-0002-9229-2113).

EIS data analysis and interpretation.

Katarzyna Bejtka (ORCID: 0000-0003-1731-5861).

Undoped-catalyst conceptualization. Electron microscopy measurements (SEM and TEM), EDX measurements, data analysis and interpretation.

Micaela Castellino (ORCID: 0000-0002-1393-4043).

XPS measurements, data analysis and interpretation.

M. Amin Farkhondehfar (ORCID: 0000-0002-5433-5653).

HPLC measurements, data analysis and interpretation.

Angelica Chiodoni (ORCID: 0000-0002-4386-842×).

XRD measurements, data analysis and interpretation.

Fabrizio Pirri.

P.I. of IIT-CSFT@Polito scientific research line.

Elena Tresso (ORCID: 0000-0001-9223-379×).

First author's supervisor.

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Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2022.106412>.

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