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Cost-effective, high-performance Ni_3Sn_4 electrocatalysts for methanol oxidation reaction in acidic environments†

Danil W. Boukhvalov, ^{ab} Gianluca D'Olimpio, ^c Junzhe Liu, ^d Cornelius Ghica, ^e Marian Cosmin Istrate, ^e Chia-Nung Kuo, ^f Grazia Giuseppina Politano, ^g Chin Shan Lue, ^f Piero Torelli, ^h Lixue Zhang *^d and Antonio Politano *^c

Methanol (CH_3OH) oxidation offers a promising avenue for transitioning to clean energy, particularly in the field of direct methanol fuel cells (DMFCs). However, the development of efficient and cost-effective catalysts for the methanol oxidation reaction (MOR) remains a critical challenge. Herein, we report the exceptional electrocatalytic activity and stability of Ni_3Sn_4 toward MOR in acidic media, achieving a performance comparable to that of commercial Pt/C catalysts. Our catalyst design incorporates Earth-abundant Ni and Sn elements, resulting in a material that is 1800 times more cost-effective than Pt/C. Density functional theory (DFT) modeling substantiates our experimental findings, shedding light on the favorable reaction mechanisms and kinetics on the Ni_3Sn_4 surface. Additionally, the as-synthesized Ni_3Sn_4 electrocatalyst demonstrates commendable durability, maintaining its electrocatalytic activity even after prolonged exposure to harsh acidic conditions.

DMFCs are attractive candidates for transportable power sources due to their superior energy density, safer storage and transportation, and ease of refuelling compared to traditional hydrogen-based fuel cells.¹ However, the widespread

commercialization of DMFCs has been limited due to the lack of efficient, stable, and cost-effective catalysts for MOR.^{2–4} Discovering cost-effective and stable catalysts in acidic environments is crucial for the advancement of DMFC technology.

The current state-of-the-art catalysts for MOR are platinum (Pt) and palladium (Pd), which often deliver onset potentials of about 450–550 mV and hold great potential application in DMFCs. However, the high cost of these precious metals is a major barrier to large-scale implementation of MOR catalysts for DMFCs. Many transition metal catalysts have been demonstrated to be active toward MOR in alkaline conditions, but MOR onset potentials of these catalysts are too high to be used in DMFCs.^{5–7} Furthermore, methanol decomposition on transition-metal surfaces generates poisoning adsorbates (especially CO^8), which hinder their catalytic activity. Therefore, developing transition metal-based catalysts with high MOR activity, stability in acid conditions, and superior CO tolerance is of great significance and importance.

Recently, various Ni-based electrocatalysts, including Ni oxides, Fe–Ni nanoparticles, and $\text{Ni}/\text{Al}_2\text{O}_3$, have demonstrated impressive MOR performance under alkaline conditions.^{6,7,9,10} Nonetheless, due to Ni's tendency to dissolve in acidic environments, reports of Ni-based electrocatalysts' MOR activity in acidic media are scarce. While a Ni metal catalyst supported on partially sulfonated polyaniline has exhibited notable MOR activity and stability in acidic condition,¹¹ pure nickel does not perform particularly well as an MOR catalyst. That being said, Ni-based alloys, characterized by their unique electronic structures and anti-corrosion properties,¹² hold potential as catalyst candidates for MOR in acidic media.

Among the various Ni-based alloys, Ni–Sn compounds represent potential candidates, especially considering that the incorporation of Sn atoms makes CO adsorption energetically unfavorable, thus totally preventing the methanation reaction.¹³ Moreover, Ni–Sn compounds are abundant and widely available, making them an attractive alternative to Pt- and Pd-based catalysts from a cost perspective.^{14–16}

^a College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, P. R. China
^b Institute of Physics and Technology, Ural Federal University, Mira Str. 19, 620002 Yekaterinburg, Russia
^c Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, 67100 L'Aquila (AQ), Italy. E-mail: antonio.politano@univaq.it
^d College of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, P. R. China. E-mail: zhanglx@qdu.edu.cn
^e National Institute of Materials Physics, Atomistilor 405A, 077125 Magurele, Romania
^f Department of Physics, National Cheng Kung University, 1 Ta-Hsueh Road, 70101 Tainan, Taiwan
^g Department of Information Engineering, Infrastructures and Sustainable Energy (DIIES), University "Mediterranea" of Reggio Calabria, Loc. Feo di Vito, 89122 Reggio Calabria, Italy
^h CNR-IOM, TASC Laboratory, Area Science Park-Basovizza, 34139 Trieste, Italy
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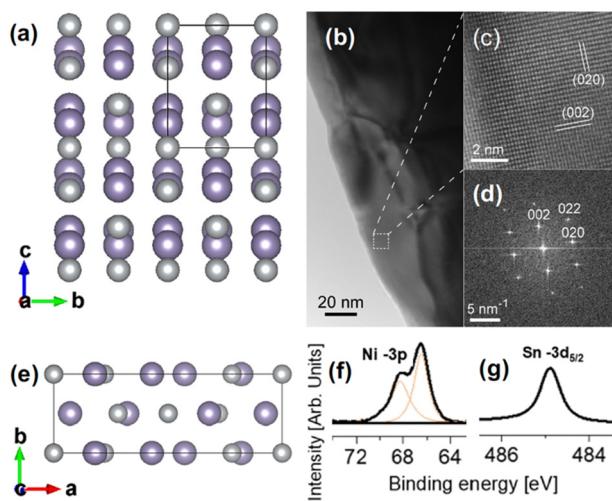


Fig. 1 (a) Top and (e) side views of the atomic structure of Ni₃Sn₄. Ni and Sn atoms are denoted by gray and purple balls, respectively. (b) TEM image of Ni₃Sn₄. Panels (c) and (d) report the HR-TEM image and the SAED pattern acquired in the region denoted by a dashed white square in panel (b). (f) Ni-3p and (g) Sn-3d_{5/2} core levels of the as-cleaved Ni₃Sn₄ crystal.

Recently, Ni–Sn nanoparticles supported on carbon substrate have been tested for MOR in alkaline solution media, which showed reasonable catalytic performance.¹⁵ However, the MOR performance of Ni–Sn compounds in acidic media has not been reported yet. Considering the potential applications in DMFCs, it is highly worthwhile to explore the MOR performance of Ni–Sn alloys with appropriate Ni ratios in acidic conditions, given their commendable corrosion resistance.^{17,18}

In this work, we synthesized Ni₃Sn₄ and employed a combination of experimental and theoretical techniques to investigate its electrocatalytic properties toward MOR in acid environments. Our findings reveal the exceptional performance of Ni₃Sn₄, including its high MOR activity, stability, and superior CO tolerance, making it a promising candidate for use in DMFCs.

Single crystals of Ni₃Sn₄ were grown by the solution-growth method (see ESI,† Section S1). Ni₃Sn₄ (Fig. 1a) belongs to the C2/m [no. 12] (monoclinic unit cell) space group. The X-ray diffraction (XRD in ESI,† Fig. S1 and S2), transmission electron microscopy (TEM, Fig. 1b), HR-TEM (Fig. 1c), and small-area electron diffraction (SAED) experiments (Fig. 1d) confirmed the expected Ni₃Sn₄ structure (ICSD # 105363), with lattice parameters $a = 12.236 \text{ \AA}$, $b = 4.063 \text{ \AA}$, and $c = 5.224 \text{ \AA}$. The presence of a single doublet in Ni-3p and a single component in Sn-3d_{5/2} core levels further confirm the presence of a single Ni₃Sn₄ phase (see also X-ray absorption spectroscopy experiments reported in ESI†).

We measured the electrocatalytic activity of the obtained Ni₃Sn₄ toward MOR in a traditional three-electrode configuration with a scan rate of 50 mV s⁻¹. In Fig. 2a, the oxidation peak at around -0.3 V vs. Hg/Hg₂SO₄ is well evident in the case of the 0.5 M H₂SO₄ + 1 M CH₃OH mixture, while it is clearly absent in the case of 0.5 M H₂SO₄ only. This finding confirms the catalytic activity of Ni₃Sn₄ towards MOR. Fig. 2b shows the

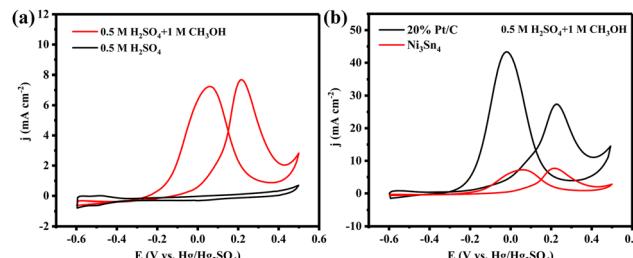


Fig. 2 (a) CV curves of Ni₃Sn₄ alloy in 0.5 M H₂SO₄ and 0.5 M H₂SO₄ + 1 M CH₃OH (scan rate of 50 mV s⁻¹), Hg/Hg₂SO₄ electrode was used as the reference electrode, graphite rod electrode was used as the counter electrode. (b) Performance comparison of Ni₃Sn₄ and commercial 20% Pt/C in 0.5 M H₂SO₄ + 1 M CH₃OH.

performance comparison between Ni₃Sn₄ and commercial 20% Pt/C in 0.5 M H₂SO₄ + 1 M CH₃OH.

Evidently, Ni₃Sn₄ exhibits a comparable onset potential to Pt/C, which is also on par with some recently reported advanced Pt-based MOR catalysts.¹⁹ This suggests that MOR takes place more readily on Ni₃Sn₄ (Fig. 2b and Table S1, ESI†).

Taking into account the bulk structure of Ni₃Sn₄, it is not surprising that it exhibits a smaller current density ($\sim 7.8 \text{ mA cm}^{-2}$) compared to Pt/C ($\sim 43.0 \text{ mA cm}^{-2}$) (Fig. 2b). When normalizing the MOR current by the electrochemical active surface areas, the current density of Ni₃Sn₄ becomes much closer to that of Pt/C (Fig. S2, ESI†). Intriguingly, an examination of the CV curves in Fig. 2b and Fig. S2 (ESI†) reveals a larger I_f/I_b ratio (I_f and I_b are the peak currents of the forward and the backward curves, respectively) for Ni₃Sn₄ than for Pt/C, suggesting an enhanced CO tolerance for Ni₃Sn₄.^{19,20} Subsequently, we performed CO stripping tests on both Ni₃Sn₄ and commercial Pt/C samples (Fig. S3, ESI†). The onset potential of CO oxidation on the Pt/C is 0.0912 V vs. Hg/Hg₂SO₄, while the onset potential of CO oxidation on the Ni₃Sn₄ sample is 0.0178 V vs. Hg/Hg₂SO₄. This result indicates a superior capability of Ni₃Sn₄ to remove adsorbed CO compared to Pt/C.

Electrochemical impedance spectroscopy (EIS) was then used to gain some insight into the MOR activity (Fig. S4, ESI†). The fitted Nyquist data shows that the charge transfer resistances (R_{ct}) of Ni₃Sn₄ and Pt/C are 6394 Ω and 3269 Ω in the mixture of 0.5 M H₂SO₄ + 1 M CH₃OH, respectively. The larger R_{ct} of Ni₃Sn₄ provides a kinetic explanation for its slightly lower MOR activity compared to Pt/C.

The durability of the Ni₃Sn₄ is also an indispensable parameter for potential applications. Firstly, the MOR process shows almost no decay after the accelerated electrochemical aging test of 1000 cycles (scan rate of 50 mV s⁻¹, Fig. 3a). Then, we carried out the chronoamperometry at 0.24 V vs. Hg/Hg₂SO₄ to evaluate the long-time stability. In the chronoamperometric test, Ni₃Sn₄ displays a more gradual decay process compared to Pt/C (Fig. 3b), which signifies the commendable durability of the as-prepared Ni₃Sn₄ electrocatalyst. Consequently, it can be concluded that the non-noble metal-based Ni₃Sn₄ exhibits a Pt-like catalytic performance for MOR in acidic environments,



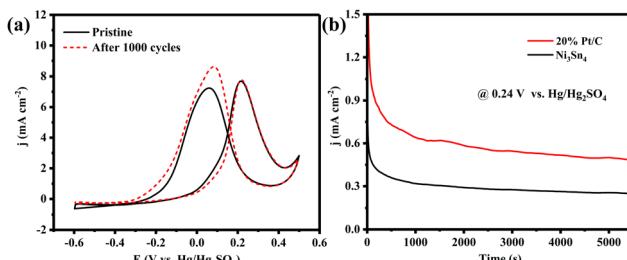


Fig. 3 (a) CV curves before and after 1000 CV scans of Ni₃Sn₄ in 0.5 M H₂SO₄ and 1 M CH₃OH solution at a scan rate of 50 mV s⁻¹ (b) chronoamperometric curves of Ni₃Sn₄ and 20% Pt/C at 0.24 V (vs. Hg/Hg₂SO₄) in 0.5 M H₂SO₄ and 1 M CH₃OH solution.

while also offering cost reductions of up to 1800 times, thanks to the substitution of expensive Pt with an alloy composed of Earth-abundant Ni and Sn elements.

In order to reveal the pathway of MOR over the Ni₃Sn₄ surface, we performed first-principles simulations. For this purpose, we used density-functional based code Quantum Espresso.²¹ For the simulation of (010) surface of Ni₃Sn₄, we used a slab of 126 atoms (see Fig. 4a). Firstly, based on recent literature on transition-metal stannides,^{22,23} we checked the possible oxidation of the surface. For this purpose, physisorption and decomposition of molecular oxygen on the (010) surface of Ni₃Sn₄ were assessed. Both these processes are very energetically favourable (−1.4 and −1.1 eV per O₂). Further oxidation of whole (010) surface (Fig. 4b) is also a very favourable exothermic process, as indicated by the corresponding energy of −3.65 eV per O₂. Thus, modelling of MOR will be performed for two types of surfaces: reduced and oxidized.

In our simulations, we considered the step-by-step migration of hydrogen atoms from methanol to the substrate. The first step of the reaction displays a significant difference between reduced and oxidized Ni₃Sn₄ surfaces. On the reduced substrate, one hydrogen atom migrates from methyl group to surface Ni-atom, resulting into formation of −OHCH₂ group attached to two Sn atoms on the Ni₃Sn₄ surface (see Fig. 4a). In the case of oxidized substrate, the first step is the formation of the −OCH₃ group covalently bonded with Sn atom on substrate surface (Fig. 4b). On the other hand, on the reduced substrate, another hydrogen atom migrates from methyl group to oxygen, resulting into formation of −OHCH₂[−] group to two Sn atoms on the substrate surface (see Fig. 4a). This difference in the reaction pathway determines the difference of the energies of the various steps of the reactions.

Calculations (Fig. 4c) indicate that, in the case of the reduced substrate, the energy cost of intermediate steps is about 1.1–1.3 eV, in qualitative agreement with the experimentally determined overpotential of about 0.9 eV (see Fig. 2 and 3). Note that the calculated energy cost is slightly larger than calculated for Pt-sites in tungsten carbide.²⁴ Contrarily, one of the intermediate steps of MOR over the oxidized surface corresponds to an energy cost above 2 eV, while the first step (Fig. 4b) has a very low energy barrier (0.3 eV). These values are similar to obtained in previous calculations for other substrates.^{25–28}

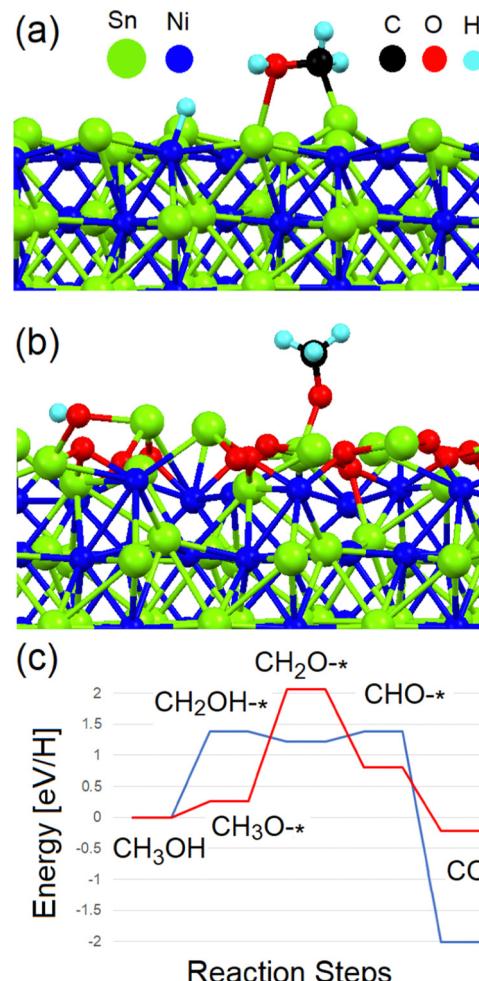


Fig. 4 (a) Optimized atomic structure of the first step of MOR on the reduced and (b) the oxidized surfaces of Ni₃Sn₄. (c) Energy diagram depicting the MOR process on both reduced (blue) and oxidized (red) surfaces of Ni₃Sn₄. The asterisk on panel (c) denotes the substrate.

Additionally, the desorption of atomic hydrogen with the formation of H₂ molecules is an exothermic process on the reduced surface (−0.3 eV), in contrast to the case of the oxidized surface. In the latter case, the removal of oxygen atoms is an endothermic process with the energy of about 0.9 eV. To merge results of the simulations with experiment, one can propose that MOR in sulphuric acid corresponds to the deoxygenation of oxidized Ni₃Sn₄, with following oxidation of methanol over reduced surface. The last step of our simulations is the evaluation of the stability of the Ni₃Sn₄ surface towards carbon monoxide poisoning. The desorption of CO from oxidized Ni₃Sn₄ surface is exothermic process with energy of −0.7 eV per CO, while an energy barrier of 0.6 eV per CO exists in the case of the reduced substrate, *i.e.*, a value more than twice smaller than in the cases of the (111) and (100) surfaces of platinum (about 1.2 and 1.4 eV per CO, respectively).²⁹ Thus, the desorption rate of CO is seven times larger for Ni₃Sn₄ than for platinum.

In conclusion, this study has shown that Ni₃Sn₄ exhibits a Pt-like catalytic performance for the MOR in acidic media,



demonstrating comparable activity and stability to commercial 20% Pt/C. Theoretical simulations provide insights into the pathway of MOR on the Ni_3Sn_4 surface, highlighting significant differences between reduced and oxidized surfaces. The desorption of CO from the oxidized surface is found to be seven times faster than that of platinum, indicating Ni_3Sn_4 as a potential alternative to platinum-based catalysts for MOR. Using Ni_3Sn_4 as a catalyst for MOR can significantly reduce the cost of raw materials compared to platinum-based catalysts, making it a promising candidate for use in various applications, including methanol fuel cells. The findings of this study also suggest the potential of Ni_3Sn_4 in other catalytic processes and encourage further exploration of its diverse applications.

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Conflicts of interest

There are no conflicts to declare.

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