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Recent advances in nanoporous materials for renewable energy resources conversion into fuels

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ABSTRACT

The continuous growth in energy production from non-renewable resources in order to meet the ever-increasing energy demand has given rise to serious environmental issues and moving toward renewable energy resources is necessary. Heterogeneous catalysts play a key role in the conversion of renewable resources into fuels and chemicals. The performance of heterogeneous catalysts is directly linked to their surface area, since the number of catalytic sites as well as the activity of each catalytic site increase with increasing effective footprint area of a catalyst. Therefore, nanoporous heterogeneous catalysts are very attractive, owing to their high internal surface areas and high density of active sites generated by curved internal surfaces. The overall catalytic performance of nanoporous heterogeneous catalysts can reach orders of magnitude higher than that of planar catalysts counterparts. This paper reviews recent progress toward the applicability of three-dimensional bulk nanoporous metals and their composites in (electro-)catalytic conversion of renewable resources into fuels and value-added chemicals. The primary focus is given to metal-based materials fabricated through dealloying. Dealloyed nanoporous metals and their composites can be used either directly as high-performance (electro-)catalysts, or indirectly as three-dimensional bulk current collectors along with poorly conducting electro-catalyst materials. Limitations of these material systems such as cost, scalability, and long-term stability in-service are discussed.

1. Introduction

Macrofoams, a class porous material with pore size on the order of tens of microns are very attractive for a variety of industrial applications owing to their unique properties. For example, aluminum macrofoam boasts a high stiffness-to-density ratio, high capacity for energy absorption during compression, high temperature resistance, electrical and thermal conductivity, good machinability and cheap production costs. Thanks to these remarkable properties, macrofoams are attractive in the construction and automotive industries, for example [1–4].

While macrofoams are common materials with known applications in industry, there is a class of materials known as nanofoams or nanoporous metals, characterized by pore and strut sizes being at the nanoscale. For a more conventional definition, the International Union of Pure and Applied Chemistry has categorized nanoporous materials into three groups, depending on the characteristic pore size: microporous (pore size under 2 nm), mesoporous (pore size between 2 and 50 nm), and macroporous (pore size above 50 nm) materials. While maintaining some attractive characteristics of cellular materials as their macrofoam counterparts, nanofoams uniquely possess properties that are beyond

the limit of macrofoams. For instance, nanofoams have seen scalable applicability in nanofiltration systems, drug delivery platforms, catalysis, sensing and actuation [5–12]. Nanoporous materials are also expected to significantly contribute to energy applications. To meet the increasing demand for renewable energy, cost-effective and scalable methods are needed for the conversion of renewable resources into fuels and value-added chemicals [13,14]. The kinetics of chemical reactions involved in fuel production can be enhanced by heterogeneous catalysts [15,16]. Furthermore, the performance of heterogeneous catalysts is directly linked to the number of catalytic sites per unit surface area: the higher the effective surface area of a catalyst, the better it performs [17]. Heterogeneous catalysts with high internal surface areas are therefore very attractive. Three-dimensional (3D) bulk nanoporous metals (NPM) represent an emerging class of materials characterized by their high specific surface area, remarkable intrinsic physical and chemical properties, and a unique combination of the mechanical robustness of “dense” materials with the intriguing properties of “nano” materials.

Thanks to these remarkable properties, 3D NPMs are very attractive in catalysis and electro-catalysis applications where they are used to

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enhance the kinetics of chemical and electrochemical reactions in two ways: (i) Either directly as (electro-)catalysts; (ii) or indirectly as electrically conducting 3D framework (NPMF) current collectors in combination with poorly conducting electro-catalyst materials, to enhance the overall charge transfer in the corresponding NPMF/electro-catalyst composites.

To date, 3D NPMs have found great advantage and applicability in the field of (electro-)catalysis for fuel production (e.g. H_2O oxidation and CO_2 reduction) and fuel consumption (e.g. methanol oxidation) [17–21]. Beside the high effective surface area of these materials, their improved performance also arises from their intrinsic chemical and physical properties such as electrical conductivity [21]. Finally, the broad range of NPMs makes it possible to design high-performance catalysts directly through the Sabatier principle, by properly selecting from volcano plots NPMs that will exhibit optimal surface interaction with the substance to convert. State-of-the-art (electro-)catalytic processes for fuel production and fuel consumption include water oxidation reaction (WOR), methanol oxidation reaction (MOR), and carbon dioxide reduction (CDR).

- (i) The water oxidation reaction (also referred to as oxygen evolution reaction – OER) is very attractive for sustainable fuels production. This is because beside the high abundance of water for large scale energy applications, electrons generated during water oxidation can reduce protons and CO_2 into H_2 and carbonaceous fuels, respectively [22]. This non-spontaneous reaction is commonly driven by an external bias voltage, and electro-catalysts are required to lower the value of this voltage.
- (ii) Direct methanol fuel cells (DMFCs) have the advantage of simple operation and high energy density, and thus applicable in automobile and portable electronics [23]. The methanol oxidation reaction is critical in DMFCs, and similarly to WORs, (electro-)catalysts are required to enhance to kinetics of MORs and lower the reaction overpotential.
- (iii) The electrochemical reduction of CO_2 into other reusable carbon fuels such as CO and CH_4 is desirable from the view of sustainability and environment protection [24–29]. However, CO_2 is a fully oxidized and one of the most stable molecule among carbon-based substances [30,31]. Thus, cost effective, high selectivity and high efficiency (electro-)catalysts that can lower thermodynamic barrier for CDR are required [30,32].

In this contribution, we will discuss recent progress toward the applicability of 3D NPMs in the above 3 fields. The primary focus will be on NPMs produced by selective alloy leaching, a process known as dealloying. After presenting state-of-the-art dealloying routes to NPM (electro-)catalysts, we will discuss recent achievements in electro-catalytic oxidation of water using metallic foams and NPM composites. Next, we will present the performance of NPMs as methanol oxidation (electro-)catalysts. Finally, the potential of NPMs as CO_2 reduction electro-catalysts will be discussed.

2. Fabrication of nanoporous metal catalysts

The most popular method for the fabrication of nanoporous metal catalysts corresponds to the conventional “dealloying” route in aqueous media. During this nanofabrication process, a sacrificial element, usually the most (electro)chemically active element, is preferentially removed from a parent alloy using an acidic or alkaline aqueous corroding medium; sometimes an external electrical bias voltage can be used to drive the dealloying process if the reactions involved are not spontaneous [33–43]. In the former case where no external electrical field is required to assist the dissolution of the sacrificial component, the leaching process is referred to as free corrosion dealloying [33]. Fig. 1a shows the typical 3D bicontinuous morphology of nanoporous gold (NP-Au) prepared by free corrosion dealloying of Au/Ag alloy and

used as catalyst for selective oxidation of methanol at low temperatures [19].

Fig. 1b depicts a similar 3D bicontinuous morphology in nanoporous silver (NP-Ag) prepared by free corrosion dealloying of a Ag/Al alloy and used as electro-catalyst for selective reduction of carbon dioxide to carbon monoxide [17]. The NP-Ag electro-catalyst from Fig. 1b was prepared from a non-equilibrium single-phase Ag/Al parent alloy following a procedure reported earlier by DeHosson et al. [34].

Besides dealloying in aqueous media, recently several new dealloying approaches have been explored: Sieradzki and Chen reported on electrolytic dealloying in Li-based nonaqueous solutions [44]; Detsi and co-workers suggested the use of Mg-based nonaqueous solutions for the selective electrolytic corrosion of Mg-rich alloys [45]; Kato and co-workers reported on free corrosion dealloying by metallic melt, a leaching process during which a molten hot metal is used as corroding medium to selectively extract the most reactive component of a parent alloy, taking advantage of the difference in enthalpy of mixing between the underlying alloy elements and the molten hot metal [46]; Chen and co-workers reported on vapor phase dealloying, during which the sacrificial phase is selectively removed by thermal evaporation [47]. Thanks to these various but complementary nanofabrication methods, a broad range of NPMs can be made for various applications including (electro-)catalysis.

3. Water oxidation

3.1. Motivation and background

The high abundance of water and the possibility to use electrons generated through water oxidation to reduce protons and CO_2 into H_2 and carbonaceous fuels, respectively [22], make the water oxidation reaction (WOR) very attractive for sustainable production of fuels and value-added chemicals. Protons reduction into H_2 is commonly referred to as hydrogen evolution reaction (HER) and when electrons used to reduce these protons are generated from the WOR, the combined HER and WOR process is referred to as water splitting. In this section we will focus on the WOR. This non-spontaneous reaction is commonly driven by an external electrical bias voltage, and like in any non-spontaneous electrochemical process, the applied electrical bias voltage is always higher than the thermodynamic potential of the reactions involved.

This difference between the theoretical and applied voltages is known as overpotential. The three primary origins of an overpotential area: (i) the internal resistance of the system; (ii) the charge transfer resistance at the solid catalyst/electrolyte interface; and (iii) the activation overpotential associated with an energy barrier to overcome before the reaction can take place. This energy barrier is significantly low in catalysts. Hence (electro-)catalysts are used to lower the overall value of the bias voltage involved in the WOR. The mechanism of electro-catalytic oxidation of water has been widely investigated [48], and high-performance water oxidation electro-catalysts have been identified [21,49–51], among which NiFe-based oxides, cobalt phosphate and cobalt borate systems have been developed [51,52].

A major fundamental challenge in the field, which will be the focus of this section, is associated with the poor electrical conductivity of water oxidation electro-catalysts (i.e. resistance overpotential). Indeed, water oxidation reaction favorably proceeds on non-metallic surfaces [53]; however non-metallic materials used as electro-catalysts suffer from very poor electrical conductivity when their characteristic structure size is not in the sub-100 nm range. This issue represents a bottleneck in the development of robust and scalable water oxidation electro-catalysts. For our porous materials systems, the fact that water oxidation takes place on non-metals also means that NPMs cannot be used directly as water oxidation (electro-)catalysts.

Fig. 1. (a) Typical 3D bicontinuous morphology of nanoporous gold catalyst at low and high magnifications, respectively. The nanoporous Au was prepared by dealloying of Au/Ag parent alloy (Reproduced from ref. [19]). (b) Similar 3D bicontinuous morphology in nanoporous silver catalyst prepared by dealloying of Ag/Al parent alloy following the procedure in ref. [34]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [17])

3.2. Nanoporous metal/metal oxide composites

To find a way around this conductivity issue, some cellular materials have been proposed as 3D electrically conducting scaffolds (see Fig. 2a reproduced from [54]). In particular, state-of-the-art water oxidation electro-catalysts have been infiltrated into the pores of commercially available 3D nickel foams as illustrated in Fig. 2b and c reproduced from [52], to design robust electro-catalysts that can generate practical currents during water oxidation [52,55–58].

Thin films of Co-based water oxidation electro-catalysts can produce a current density of $\sim 1 \text{ mA/cm}^2$ at $\sim 410 \text{ mV}$ overpotential near neutral pH [21,50]. As discussed earlier, this overpotential means that more energy is required than thermodynamically determined in order to drive a redox reaction. However, when these Co-based electro-catalysts are electrodeposited onto a 3D nickel foam scaffold to enhance their electrical conductivity, the corresponding water oxidation current density is increased from of $\sim 1 \text{ mA/cm}^2$ to $\sim 100 \text{ mA/cm}^2$ at 363 mV overpotential [21,52].

Another class of high-performance water oxidation electro-catalysts corresponds to NiFe oxides [21,49,59–62]. Thin films of NiFe-based water oxidation electro-catalysts can deliver a current density of $\sim 10 \text{ mA/cm}^2$ at $\sim 350 \text{ mV}$ overpotential in 1 M alkaline solutions [21,49]. However, when NiFe-based water oxidation catalysts are grown onto 3D nickel foams to enhance their electrical conductivity,

they only require 240 mV overpotential (instead of $\sim 350 \text{ mV}$) to achieve a current density of $\sim 10 \text{ mA/cm}^2$ in 1 M NaOH solution [21,55]; and they can deliver a current density of $\sim 500 \text{ mA/cm}^2$ in 10 M KOH [21,56].

Despite this enhancement when Ni foams are used as 3D substrates and water oxidation electro-catalysts supported onto 3D nickel foams, there are advantages and disadvantages associated with the use of these metal foams, as reported previously by Detsi et al. [21]: As major advantage, a nickel foam with its high intrinsic electrical conductivity can successfully act as effective 3D bulk current collector for the electro-catalyst deposited onto its pore walls. In addition, the porous architecture of open cell nickel foams favors an effective transfer of ionic species and gas molecules at the catalyst/electrolyte interface [21]. The primary disadvantage of using commercially available nickel foams for these types of applications corresponds to the very large pore sizes of macro-foams, which is commonly in the submillimeter to millimeter range [21]. Consequently, as pointed out in ref. [21], the specific surface area of open cell nickel foams is very low [21,63–65]. In contrast to nickel foams, 3D nanoporous structures can exhibit much larger interfacial surface areas, since the specific surface area scales inversely with the average pore size [21,34,66,67]. Detsi et al. used dealloying to produce a high-performance, robust, and ultrafine mesoporous NiFeMn metal/metal oxide water oxidation electro-catalysts with average ligament size on the order of $\sim 10 \text{ nm}$, BET surface area of $43 \text{ m}^2/\text{g}$ and high

Fig. 2. (a) Open cell aluminum foam, (Reproduced from [54]). (b, c) Open-cell nickel foam coated with cobalt-based water oxidation electro-catalyst at low and high magnification, respectively. (Reproduced from [52])

Fig. 3. (a) SEM of the fracture cross-section of a 300 μm-thick nanoporous NiFeMn-based electro-catalyst. (b) TEM showing a typical ligament in the NiFeMn-based electro-catalyst. The ligament is covered with a few nanometer-thick oxide layer as illustrated by the dashed yellow line. (c) Linear sweep voltammograms obtained from the nanoporous NiFeMn metal/metal-oxide catalyst (red) and a dense NiFeMn catalyst counterpart (black) at a sweep rate of 1 mV s^{-1} in 0.5 M KOH. The nanoporous catalyst delivers 10 mA cm^{-2} at only 200 mV (inset), while the dense catalyst counterpart does not achieve 10 mA cm^{-2} until 430 mV (sweep rate of 1 mV s^{-1} ; 0.5 M KOH). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [21]).

electrical conductivity [21]. This was achieved by partial removal of Mn from Mn-rich ternary alloys with composition $\text{Ni}_{15}\text{Fe}_{20}\text{Mn}_{65}$ at.%.

The typical microstructure of the dealloyed ternary material with final composition $\text{Ni}_{60}\text{Fe}_{30}\text{Mn}_{10}$ at.% is shown in Fig. 3a at low and high magnifications. A mixed native oxide (i.e. Ni oxide, Fe oxide and Mn oxide) covers the internal surface of this mesoporous alloy as depicted by the high-resolution transmission electron microscopy (TEM) image of Fig. 3b. This NiFeMn mixed oxide acts as electro-catalyst for water oxidation. Furthermore, electrons generated during water oxidation on this oxide nanocoating are effectively collected by the inner NiFeMn metallic component of this metal/metal oxide composite system. The unique combination of small ligaments and pores size ($\sim 10 \text{ nm}$), high BET surface area ($43 \text{ m}^2/\text{g}$), open porosity for effective mass transfer at the catalyst/electrolyte interface, high bulk electrical conductivity for effective current flow through the electro-catalyst, makes it possible to use unprecedented thick films ($\sim 300 \mu\text{m}$) with a high density of active catalyst sites per unit electrode area, resulting in very high current densities during water oxidation as shown in Fig. 3b, reproduced from [21]. For the sake of illustration, common unsupported non-precious metal oxygen-evolution catalysts require at least $\sim 350 \text{ mV}$ overpotential to oxidize water with a current density of 10 mA/cm^2 in 1 M alkaline solution. The nanoporous NiFeMn/NiFeMn oxide composite made by selective alloy corrosion exhibits an electro-catalytic activity toward water oxidation of 500 mA/cm^2 at 360 mV overpotential and is stable for over eleven days in 1 M KOH [21].

Zhang and co-workers also used the dealloying strategy to derive a high-performance mesoporous NiFe-based water oxidation electro-catalyst (see Fig. 4) during selective removal of Al from $\text{Al}_{97}\text{Ni}_x\text{Fe}_{3-x}$ alloys [68]. Their composite material required only $\sim 244 \text{ mV}$ overpotential to oxidize water with a current density of 10 mA/cm^2 in 1 M alkaline solution [68].

Sun and co-workers used dealloying to produce high-performance NiFeCu-based metal/metal oxide water oxidation electro-catalysts during partial removal of Cu from co-deposited Cu-rich NiFeCu ternary alloys with elemental ratio Ni:Fe:Cu to be 10:1:21 [69]. The corresponding metal/metal oxide nanocomposite structure (with metallic core and oxide shell) required only $\sim 180 \text{ mV}$ overpotential to oxidize water with a current density of 10 mA/cm^2 in 1 M alkaline solution [69].

3.3. Critical remarks

The use of non-precious elements such as Ni and Fe in high-performance water oxidation heterogeneous nanoporous catalysts is very attractive for large scale applications. The fact that these catalysts are composite materials in the form of metal/metal oxides prevent the nanoporous metal scaffold from coarsening during water oxidation onto the oxide coating. Although ultra-small pores (e.g. $\sim 10 \text{ nm}$ from the structure in Fig. 3a) are needed for high specific surface areas, it is expected that during water oxidation, O_2 gas produced in the bulk of thick nanoporous catalysts (e.g. the $\sim 300 \mu\text{m}$ thick nanoporous film from ref. [21]) will not easily escape from this bulk. A build-up of O_2 gas inside the bulk of the electrode material is susceptible to increase the internal resistance of the system, which in turn will increase the overall water oxidation overpotential. A possible solution to this problem is the design of hierarchical nanoporous electro-catalyst, where macro- and mesopores coexist. The mesopores will then provide the large surface area needed for the water oxidation reaction, while the macropores will allow O_2 gas to escape from the bulk. To our opinion, such an architecture with bimodal porosity represents the “ideal” material design.

4. Methanol oxidation

4.1. Motivation and background

Due to their high efficiency and environmental-friendliness, fuel cells have gained increased attention in the field of electrochemical energy storage and conversion [70,71]. Among these, direct methanol fuel cells (DMFCs) have the advantage of simple operation and high energy density, and thus applicable in automobile and portable electronics [23]. The methanol oxidation reaction (MOR) is critical in DMFCs, and (electro-)catalysts are required to enhance the kinetics of this reaction. The most common electro-catalysts are Pt-based materials [72,73]. However, Pt-based catalysts suffer from poisoning by CO. In addition, there are intermediates during the methanol oxidation, which causes low efficiency [74,75]. Therefore, it is necessary to find alternative catalysts that do not have such drawbacks while displaying high catalytic activities and good stability.

Fig. 4. (a, b) SEM images of the $\text{Al}_{97}\text{Ni}_2\text{Fe}_1$ alloy ribbon after being immersed in the 1 wt% HF aqueous solution for 8 min. (c) Photograph of the as-dealloyed $\text{Ni}_2\text{Fe}_1\text{O}$ powders.

(Reproduced from ref. [68])

4.2. Nanoporous gold

NP-Au has been explored as metal oxidation electro-catalyst. A typical cyclic voltammograms (CV) of NP-Au in 0.5 M KOH solution with and without 1 M CH_3OH , as reported by Ding and co-workers is shown in Fig. 5 [20]. It can be seen that the electrochemical current is significantly enhanced upon addition of methanol in the electrolyte [20]. In other words, NP-Au electrode is highly active toward methanol electro-oxidation or electro-reduction.

It was reported that electro-oxidation of methanol happens at two potential regions, namely -0.5 to 0.4 V (vs SCE) and 0.44 to 0.8 V (vs SCE), based on different mechanisms [20]. At lower potentials, four-electron transfer reaction happens [76,77]:

while six-electron transfer process happens at higher potentials and methanol is oxidized into carbonates [76,78]:

The four-electron process (Eq. (1)) takes place in combination with both the chemisorbed OH^- and the formation of pre-oxidation species [20,76,78]. As potential reaches -0.5 V, OH^- anions start to chemisorb on the NP-Au surface, which onsets the methanol oxidation process; As the potential sweeps positively, more OH^- will adsorb on the NP-Au surface and react with gold surface atoms to form “pre-oxidation precursors” such as $\text{Au-OH}_{\text{ads}}^{(1-m)-}$, where “m” is the charge-transfer coefficient that varies between 0 and 1 [20,78].

Fig. 5. Cyclic voltammograms (CVs) of NP-Au electrodes in 0.5 mol dm^{-3} KOH solutions with and without 1.0 mol dm^{-3} CH_3OH . The potential scan rate was 10 mV s^{-1} .

(Reproduced from ref. [20]).

This partially oxidized NP-Au will greatly enhance the oxidation of methanol, as shown in the first peak in Fig. 5 [20]. However, as potential increases, $\text{Au-OH}_{\text{ads}}^{(1-m)-}$ will be consumed to form relatively dense and ordered gold oxides, and the exhaustion of $\text{Au-OH}_{\text{ads}}^{(1-m)-}$ will slow down and eventually stop the methanol oxidation reaction [20]. Thus, an inhibition to the methanol oxidation initiates at around 0.25 V (vs SCE), as can be seen from Fig. 5 [20]. At more positive potentials, the methanol oxidation reaction is again activated through those earlier formed gold oxides [79]. Herein the six-electron transfer reaction happens (Eq. (2)), providing an alternative reaction channels for methanol oxidation [20]. It also allows reaction intermediates produced at lower potentials to be further oxidized, thus eliminating potential catalyst poisoning [20]. This is a great advantage over Pt-based material. Also, the oxidation was observed to occur at less positive potentials, which agrees with the work of Borkowska et al. [80].

As potential sweeps negatively, first there will be electrochemical reduction of gold surface oxides corresponding to a reduction peak at around 0.04 V (vs SCE) [20]. With the removal of oxide, $\text{Au-OH}_{\text{ads}}^{(1-m)-}$ is recovered and initiating four-electron oxidation process at around 0 V (vs SCE) [76,78]. Although Ding and co-workers found the greatly enhanced catalytic activity of NP-Au for methanol oxidation, they also observed the decrease in activity upon long-time cycling [20].

Since there is no catalyst poisoning, this decrease should be attributed to the change of surface structure [20]. As shown in Fig. 6, the starting NP-Au has an average pore/ligament size around 12 nm, while after cycling it seriously coarsens to more than 40 nm. They have concluded that the coarsening and clogging of pores result in the loss of active surface area, which in turn decrease the electro-activity of NP-Au [20].

Weissmüller and co-workers [81] held two doubts upon re-examination the results of Zhang et al.: (1) The conclusion of the six-electron reaction product carbonate (CO_3^{2-}) was based on assumptions for planar electrodes during ethanol oxidation [76,77], and was not supported by experimental evidence. (2) The performance of NP-Au as an electro-catalyst compared to other porous gold materials with different activities [74,82,83] is unknown.

It is suggested that NP-Au properties vary with the dealloying techniques [84], which result in different surface structure [85] and surface-located Ag clusters [86]. Therefore, Weissmüller and co-workers prepared three types of NP-Au, namely through mild and harsh potentiostatic dealloying as well as open-circuit corrosion [81]. Fig. 7 shows the scanning electron microscopy (SEM) images of the three type NP-Au, and the corresponding sample properties are summarized in Table 1 [81].

As can be seen from Table 1, NP-Au (A) has the smallest pore/ligament size that corresponds to the highest surface area [81]. It is known that small pores and ligaments feature a higher curvature [87],

Fig. 6. SEM images of an NPG electrode measured before (a) and after (b) electro-oxidation of methanol. Scale bars in two SEM images are 100 nm. Insets in two images show the change of the colour of NPG before and after the electro-catalytic reaction. (Reproduced from ref. [20]).

which is in turn associated with more low-coordinated atoms. Low-coordinated sites usually display higher activity [88], but the NP-Au (A) here shows the lowest current ($42 \mu\text{A}/\text{cm}^2$); On the other hand, samples with less low-coordinated sites show much higher current density ($101 \mu\text{A}/\text{cm}^2$ for NP-Au (B) and $127 \mu\text{A}/\text{cm}^2$ for NP-Au (C)) [81]. Note that these values are within the range of previously reported results, namely $22 \mu\text{A}/\text{cm}^2$ for Xu et al. [83], and $87 \mu\text{A}/\text{cm}^2$ for Zhang et al. [20]. The poor activity of NP-Au (A) is attributed to the inefficient methanol saturation inside the nanopores, meaning that the smaller pores suffer more from the transport control [81].

As shown in Fig. 8 (reproduced from ref. [81]), the selectivity for HCHO decreases as residual Ag (X_{Ag}) increases. In other words, NP-Au (A) promotes four-electron transport process (Eq. (1)) over two-electron transport process with increasing X_{Ag} [81].

However, the authors found that indeed X_{Ag} and selectivity is not directly connected [81]. Instead, since X_{Ag} and bulk ligament size (L_{B}) are interrelated such that smaller ligaments contain more Ag [84], more residual Ag results in an increased transport limitation. Thus, the fast-interfacial reaction, i.e. the two-electron oxidation to HCHO [89] is more strongly affected than the slower four-electron oxidation to HCOO^- [81]. Note that the authors here did not find carbonate as a product [81].

Methanol can also be oxidized to methyl formate in the presence of O_2 . Wittstock et al. showed that for stoichiometric compositions of methanol and O_2 , under room temperature the selectivity to methyl formate is almost 100% with 10% conversion of methanol [19]. Upon increasing the temperature to 80°C , the conversion increases to 60% while remaining high selectivity (97%) [19].

Model studies [90] reveal that methanol is activated by surface oxygen, and will be eventually oxidized to CO_2 if O_2 is in excess. The mechanism is shown in Fig. 1a above. This work is indicative since the product here, namely methyl formate, is the precursor for formic acid, formamide and dimethyl formamide, and thus embraces various applications [91].

In addition to using pure NP-Au as catalyst, hybrid material systems such as Pt/NP-Au catalyst also exhibit high performance over methanol electro-oxidation. Ding and co-workers obtained excellent performance toward methanol and CO oxidation using Pt-decorated NP-Au leaf in acidic solutions [92]. Similar result was obtained by Zhang et al., where Pt/NP-Au catalyst displays more negative onset potential for methanol oxidation as well as significantly enhanced current density [20]. This may shed light on possibilities for alternative ultralow precious metal loading catalyst to traditional ones, and is promising in green-energy applications [92].

4.3. Nanoporous palladium

Zhang and co-workers obtained a novel structure, namely nanoporous palladium (NP-Pd) rod (see Fig. 9) through dealloying of Pd-Al alloy in acid [93].

It was loaded onto a freshly polished glassy carbon as a catalyst for methanol electro-oxidation [93]. Cyclic voltammetry (CV) shows two anodic peaks, one at positive potential sweep and the other at negative potential sweep, respectively (Table 2) [93]. The peak located in the positive scan is correlated to the oxidation of chemisorbed methanol molecules [94–96]. The negative scan peak is attributed to methanol oxidation after Pd surface oxide is reduced [93,97], same scenario as methanol oxidation using NP-Au [20]. Similar CV trend, as well as greatly enhanced catalytic activity is also observed with NP-Pd obtained from Pd-Al alloy in basic solution [98].

As can be seen from Table 2, the relation between NP-Pd mass loading and peak current density is not linear [93]. It indicates that there is an optimal metal dispersion ratio in the carbon matrix, which will result in largest electrochemical active surface area (EASA) [93]. When the mass loading exceeds the optimal ratio, metal particles agglomerate and reduce the amount of three-phase reaction interface, thus catalytic activity decreases [93]. Similar trend is also observed for other material systems [99,100].

4.4. Critical remarks

Up to now, various nanostructured materials have been investigated as potential candidates for high-performance methanol oxidation catalysts. Conventional approaches include the use of nanoparticles supported on conductive substrate such as carbon-supported Au-Pt nanoparticles [101–103]. One potential drawback of using such approach originates from the difficulty of achieving effective particle dispersion: various surface chemistry techniques are necessary for nanoparticles to be uniformly dispersed within the conductive support matrix, and during such surface modification process it is possible to cause structural damage to the support, leading to loss of conductivity and thus lowering the performance [104,105]. On the other hand, nanoporous metal catalysts are self-supported, with good conductivity and mechanical stability, thus eliminating the risk of having conductive support lowering the overall catalytic activity.

The 3D NP-Au and NP-Pd electro-catalysts have the advantage of effectively suppressing poisoning from CO during methanol oxidation, which is otherwise the main drawback of using Pt-based catalysts. Although they display high electro-catalytic performance, the porous structure of metal will eventually coarsen in aqueous solutions, which

Fig. 7. Scanning electron micrographs of NP-Au samples prepared by A: potentiostatic dealloying in HClO_4 , B: potentiostatic dealloying in HNO_3 and by C: open-circuit dealloying in HNO_3 . Left two columns: cross-sections after sample cleavage. Right two columns: top-views onto the flat sample surface. Cross-views and top-views refer to the state after dealloying (first and third column) and after ten cyclic voltammetry scans in 1 M KOH + 1 M CH_3OH (second and fourth column). All scale bars: 100 nm.

(Reproduced from ref. [81]).

results in the decrease of active surface area and therefore poses a challenge for long-term cycling stability [20]. In addition, the pore size should be controlled within an optimal range where mass transport can be effectively facilitated [81]. Otherwise the overall performance could be limited by mass transport. Last but not least, the high cost of material

is also a limiting factor for large scale applications.

Table 1
Properties of NP-Au and Au electrode.

	NP-Au (A)	NP-Au (B)	NP-Au (C)	Au
L_B (nm) ^a	28	51	69	–
	34	46	67	–
L_s (nm) ^a	8	9	58	–
	16	26	58	–
X_{Ag-EDX} (at.%) ^a	3.6	0.1	0.8	–
	4.7	0.2	0.3	–
X_{Ag-XPS} (at.%) ^a	15.0	16.1	6.7	–
	14.4	9.1	7.2	–
C (mF)	48.6	32.2	6.4	0.2
A (cm ²)	1216.2	805.0	161.0	5.2
A_m (m ² /g)	7.2	4.7	1.0	0.003
I_p/A (μA/cm ²)	(1st) 42.0 (10th) 38.4	101.1 92.3	119.4 109.8	73.8 –
E_p (mV)	(1st) 550 (10th) 504	532 507	420 403	280 280
C_{HCHO} (μM)	75.2	303.4	87.9	236.4
C_{HCOO^-} (μM)	2613.0	4095.9	938.4	1288.3

^a Two values are provided with upper ones corresponding to values before MEO (methanol oxidation) and lower ones after MEO.

Fig. 8. Fraction of HCHO on the total product amount (HCHO + HCOO[−]) in dependence on the bulk ligament size, L_B . The corresponding increase of x_{Ag} (from EDX and XPS after cycling) is indicated by the arrow. (Reproduced from ref. [81])

5. Carbon dioxide reduction to carbon monoxide

5.1. Motivation and background

It goes without saying how essential it is to bring down the concentration of the CO₂ greenhouse gas [24,25]. This can be achieved through electrochemical reduction of CO₂ into other reusable carbon fuels such as CO and CH₄ [26–29]. However, CO₂ is a fully oxidized and one of the most stable molecule among carbon-based substances [30,31]. For example, the formation of its first reduction reaction intermediate, namely CO₂[−], in aqueous solution requires up to −1.9 V vs standard hydrogen electrode (SHE) [30,32]. This very negative potential creates high thermodynamic energy barrier as well as sluggish kinetics for overall reduction process. Thus, it brings us the challenge of how to develop a cost effective, high selectivity and high efficiency

catalyst that can function in aqueous solution [106].

Aside from the various potential reduction products of CO₂, herein we focus on CO₂ reduction to CO, which is one of the reduction pathways that attracts most attention and is a promising route for clean energy [17]. It is demonstrated that among noble metals, Au and Ag have the highest catalytic activities for CO₂ reduction to CO [30]. To further improve the performance, recent research has been devoted to developing various nanostructured electro-catalysts, which demonstrate not only huge surface reactive area but also enhanced intrinsic activity [107–112]. Here, we illustrate how nanoporous Ag and Au can be used as highly selective efficient catalyst for CO₂ reduction to CO in aqueous media, while highlighting the advantages of nanoporous structure over the other nanostructured materials.

5.2. Mechanism of electrochemical reduction of carbon dioxide to carbon monoxide

The overall reduction reaction of CO₂ to CO is stated in Eq. (3) [30]. The potential value is estimated from thermodynamic data in aqueous media at 25 °C [113].

It is commonly accepted that the above reduction process on metal surfaces can be divided into two steps, with the initial step being one-electron transfer to form adsorbed CO₂[−] (Eq. (4)) [18]:

The standard reduction potential for the CO₂/CO_{2ads}[−] couple is very negative (−1.9 V vs SHE) [30,114], meaning that in most cases (i.e. for polycrystalline metal film) the initial step is acting as the rate determining step. However, this can be shifted to more positive values if there are specific interactions between the adsorbed CO₂[−] radical and the surface atoms of the metal electrode [18,115]. The second step is the reaction intermediate CO_{2ads}[−] with two protons and another electron to form the final product CO. This can be further divided into three sub-sequential steps [18,116]:

Eq. (5) is a chemical step involving protonation of CO_{2ads}[−] to form COOH_{ads} intermediate [117]. Herein HCO₃[−] acts as the proton source since it has much lower pK_a than water [116]. Eqs. (6) and (7) are the processes associated with the formation of final product and its desorption [18].

5.3. Nanoporous silver

Among various metal catalysts, silver is one of the most investigated and promising material due to its excellent CO₂ to CO selectivity (above 80%) along with relatively reasonable cost [30,118]. In addition, due to its all-inorganic nature, it is expected to be more stable under harsh catalytic environments than homogeneous catalysts [17,119,120]. Recently, several silver-based nanostructured electro-catalysts with enhanced performance have been developed under various experimental conditions [106,121]. Herein, we focus on introducing nanoporous silver (NP-Ag) as an efficient and highly selective catalyst for CO₂ to CO conversion. NP-Ag can be obtained through different methods. De-Hosson and co-workers reported on the fabrication of ultrafine NP-Ag with structure size in the range of 30 nm by selective removal of Al from non-equilibrium (i.e. quenched) single-phase Ag/Al parent alloys [34]. Lu et al. [17] used this procedure to fabricate NP-Ag with ligament size ~50–200 nm for CO₂ reduction (Fig. 1b). Deng et al. [122] studied the tunability of pore size using catalytically driven reaction. Hsieh et al.

Fig. 9. (a–c) SEM and (d) TEM images showing the microstructure of the NP-Pd rods through chemical dealloying of the $\text{Al}_{80}\text{Pd}_{20}$ alloy in the 5 wt% HCl solution. (e) EDX spectrum showing the composition of the NP-Pd rods. (Reproduced from ref. [93])

Table 2

CV parameters for methanol oxidation on NP-Pd rods.

NP-Pd rods loading (mg/cm ²)	E_{op} (mV)	Positive scan		Negative scan	
		j_p (mA/mg)	E_p (mV)	j_p (mA/mg)	E_p (mV)
0.2	−404	166.94	−80	89.49	−143
0.4	−401	223.52	−42	146.18	−123
0.6	−400	208.20	−22	129.30	−117
0.8	−392	129.22	−28	104.74	−109
1.0	−390	118.61	−17	113.47	−89
1.2	−367	99.68	−22	90.01	−89

[18] used oxidation-reduction method in the presence of chloride anions for NP-Ag fabrication (Fig. 10). Yoon et al. [123] prepared mesostructured Ag inverse opals (Ag-IO) by replication of colloidal polystyrene thin films on Au-coated glass slides. Note that this fabrication process is “selective leaching” of templates but not a typical dealloying process [123]. The Ag-IO exhibits uniform surface structure, porosity and tortuosity (Fig. 11) [123]. Those porous structure was found to exhibit exceptional activity, not only due to the extreme increase in surface area for catalytic reaction, but also resulting from creation of highly curved internal surface which contains highly active step sites for CO_2 conversion [118].

The performance of NP-Ag catalyst is tested in CO_2 -saturated KHCO_3 electrolyte under various overpotentials. Gas-phase products are collected and analyzed using gas chromatography (GC). Greatly enhanced Faradaic Efficiency (FE) is observed under low overpotentials, along with modified selectivity and cycling stability [17,18] (Figs. 12 and 13). The performance of NP-Ag catalyst is also compared with that of Ag-foil and other Ag nanostructures as potential CO_2 electro-catalysts [17] (Table 3). It is demonstrated that NP-Ag exhibits significant advantages over other types of silver catalysts under aqueous environments in both overall and per surface site activity [17].

Tafel analysis is performed to further explore kinetics of CO_2 reduction on the NP-Ag catalyst surface (Fig. 14) [17]. For Ag foil (polycrystalline Ag) it has an Tafel slope of 132 mV dec^{-1} , which is close to the theoretical value (118 mV dec^{-1}) and the value ($\sim 140 \text{ mV dec}^{-1}$) obtained under similar experimental conditions [17,18,30,124,125]. This indicates that for Ag foil the rate determining step is CO_2 gaining an electron to be CO_2^- [17]. For NP-Ag, on the other hand, the Tafel slope of 58 mV dec^{-1} indicates that it has a fast electron transfer step, followed by a non-electron transfer rate-determining step [17,126]. This further confirms that NP-Ag surfaces are better in stabilization of CO_2^- intermediate [17]. Similar results have been reported for Ag system [18] (Fig. 15) as well as other systems [124]. It is also suggested that for NP-Ag, the real rate-determining step is the

Fig. 10. (a) Schematic illustration of the formation of as-prepared AgCl and Ag nanocorals. SEM images of (b) untreated Ag foil, (c) as-prepared AgCl after 12 h oxidation, and (d) Ag nanocorals. High-magnification SEM images of (e) as-prepared AgCl after 12 h oxidation and (f) Ag nanocorals. (Reproduced from ref. [18])

Fig. 11. (a) Top down (b) and cross-sectional SEM images of a Ag-IO film prepared by passing a 1 C cm⁻² Ag deposition charge. (c) Normalized X-ray diffraction peak for the Ag (111) reflection and (d) normalized cyclic voltammograms of thallium UPD and stripping for nominally planar Ag films (black) and Ag-IO samples prepared by passing of 0.5 C cm⁻² (red), 1 C cm⁻² (green), and 2 C cm⁻² (blue) Ag deposition charges. Voltammograms were normalized with respect to the -0.03 V peak. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [123])

Fig. 12. Electro-catalytic performance of NP-Ag. CO₂ reduction activity of NP-Ag and polycrystalline silver at (a) -0.60 V, and NP-Ag at (b) -0.50 V and (c) -0.40 V versus RHE. Total current density versus time on (left axis) and CO Faradaic efficiency versus time (right axis). (Reproduced from ref. [17])

migration of HCO₃⁻ to the surface sites inside the pores of NP-Ag, where HCO₃⁻ is acting as proton donor for the second electron transfer process [17]. In addition, it is demonstrated that NP-Ag displays a higher intrinsic activity over polycrystalline Ag, which may result from the fact that the NP-Ag catalyst contains a higher density of step sites with possibly higher-index facets supported by the highly curved surface [127,128], and the presence of halides (i.e. chloride ion) on the Ag electrode surface or in the proximity of the solid-solution interface will further promotes the selectivity and activity of the CO₂ electro-reduction reaction [18].

5.4. Nanoporous gold

Gold is the most active catalyst for CO₂ reduction to CO among common metals, operating at the lowest overpotential and displaying high selectivity (~87%) [30]. However, due to its high material cost and low abundance it is not suitable for large-scale applications. Several works focusing on reducing CO₂ to CO using gold nanoparticles (Au-

Fig. 13. (a) Total current density, (b) CO current efficiency, and (c) H₂ current efficiency, measured in CO₂-saturated 0.1 M KHCO₃ at different potentials (iR-corrected), for Ag foil (hollow black square), Ag nanoparticles (NPs, hollow blue triangle), and Ag nanocorals (red sphere). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [18])

Table 3
Summary of silver electro-catalysts for CO₂ reduction.

Material	Electrolyte	pH	Over-potential (mV)	j_{CO} (mA cm ⁻²)	j_{CO} (mA/mg)	BET surface area (cm ²)	Electrochemical surface area (cm ²)	Cell type	Ref
Polycrystalline Ag	0.1 M NaHCO ₃ /CO ₂	7.2	840	~4.1	N/A	2	N/A	A	[30]
Polycrystalline Ag	0.5 M KHCO ₃ /CO ₂	7.2	490	0.005	4.8×10^{-5}	2	~16	A	[17]
Polycrystalline Ag	0.5 M KHCO ₃ /CO ₂	7.2	390	Negligible	Negligible	2	~16	A	[17]
Ag nanowire	0.5 M KHCO ₃ /CO ₂	7.2	390	Negligible	Negligible	~33	~37	A	[17]
1 mg cm ⁻² loading									
Ag nanoparticle	0.5 M KHCO ₃ /CO ₂	7.2	390	0.022	0.022	71	~69	A	[17]
Ag nanoparticle	0.5 M KHCO ₃ /CO ₂	7.2	390	0.215	0.0215	710	~674	A	[17]
Ag nanoparticle	EMIM-BF ₄	N/A	170	~0.61	0.091	N/A	N/A	B	[106]
Ag nanoparticle	EMIM-BF ₄	N/A	670	~0.92	0.137	N/A	N/A	B	[106]
Ag nanoparticle	1 M KOH/CO ₂	N/A	N/A	~1 (–1.4 V vs Ag/AgCl)	~1 (–1.4 V vs Ag/AgCl)	N/A	N/A	B	[109]
Ag nanoparticle	1 M KOH/CO ₂	N/A	N/A	~3 (–1.4 V vs Ag/AgCl)	~3 (–1.4 V vs Ag/AgCl)	N/A	N/A	B	[109]
Ag pyrazole/carbon	0.5 M KHCO ₃ /CO ₂	7.2	390	8	0.1989	2852	~2650	A	[17]
Nanoporous Ag

Fig. 14. Tafel analysis. Overpotential versus CO production partial current density on polycrystalline silver and NP-Ag. (Reproduced from ref. [17])

Fig. 15. Tafel plot at different overpotentials η (iR-corrected) as a function with the CO partial current density j_{CO} , on Ag foil (hollow black square), Ag NPs (hollow blue triangle), and Ag nanocorals (red sphere). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [18])

NP) have been reported [110,124,129]. Hall et al. reported using Au inverse opal (Au-IO) with uniform pore distribution for highly selective CO₂ to CO conversion [130]. They claimed enhanced catalytic performance with increasing porous Au film thickness, achieving 99% selectivity for CO evolution at overpotentials as low as 0.4 V [130].

The Au-IO is obtained using similar method as mentioned previously [123]. Again, it should be noted that although the nanoporous structure is obtained through selective leaching of templates, this process is different from typical dealloying defined previously [130]. SEM images suggest formation of ordered porous network extending uniformly from the surface of the film to the underlying Au substrate (Fig. 16) [130]. X-ray diffraction (XRD) and underpotential deposition (UPD) reveal similar grain structure and surface termination [130].

The increased selectivity for CO revolution over Hydrogen evolution reaction (HER) is suggested to stem from the generation of diffusional gradients within the pores [130]. It is shown that the specific activity for CO evolution displays roughly log-linear scaling versus applied

Fig. 16. Top down (a) and cross sectional (b) SEM images of Au-IO thin film. Grazing incidence XRD (c) of 0.5 (green), 1.6 (blue), 2.7 (red) μm thick Au-IO samples showing the Au (111) Bragg diffraction peak. Cyclic voltammograms (d) of 0.5 (green), 1.6 (blue), 2.7 (red) μm thick Au-IO samples recorded in 0.1 M NaOH containing 0.01 M $\text{Pb}(\text{OAc})_2$ (10 mV s^{-1} scan rate). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [130])

Fig. 17. Specific activity for CO (a) and H_2 (b) evolution for 0.5 (green triangles), 1.6 (blue circles), 2.7 (red squares) μm thick Au-IO samples evaluated in CO_2 -saturated 0.1 M KHCO_3 electrolyte, pH 6.7. Error bars represent standard deviations of three independently synthesized Au-IO samples for each thickness. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Reproduced from ref. [130])

overpotential, while the HER polarization curve is sigmoidal (Fig. 17) [130]. The decrease in the specific activity for CO evolution for the thickest sample is attributed to the onset of transport limitations [130]. Nevertheless, the inhibition of HER is principally driven by increased alkalinity that develops within the porous network during catalysis [130].

It is also suggested that this increased alkalinity serves to directly slow the rate of HER via local depletion of competent proton donors such as HCO_3^- [130]. In addition, computational and experimental data indicate that hydroxide adsorption promotes CO binding to Au [131–133]. Thus, increased alkalinity may also indirectly suppress HER through enhanced CO adsorption [130].

5.5. Critical remarks

It is demonstrated that nanoporous structures of Au and Ag not only greatly enhances the specific surface area, but also generates a large number of highly active step sites for CO_2 conversion through the

curved internal surface [134]. This leads to total electro-catalytic activity even orders of magnitude higher than planar material at a moderate overpotential [134]. However, Au and Ag are not suitable for large-scale applications due to their high costs. On the other hand, some earth-abundant non-precious metal including Zn can selectively convert CO_2 into CO [134,135]. Several Zn-based nanostructured electro-catalysts with modified performance have been developed recently [134,136,137]. However, there still exists difficulty in introducing nanoporosity into Zn metal electro-catalyst through dealloying due to the highly reactive nature of Zn.

6. Outlook and conclusions

In this contribution, after an overview of common selective leaching strategies for the fabrication of 3D nanoporous materials, the applicability of these materials as heterogeneous (electro)catalysts for the conversion of renewable energy resources into fuels and other valuable chemicals is discussed. The high internal surface area, high density of

active catalytic sites, and remarkable intrinsic properties of these 3D nanoporous materials make them very attractive for large scale applications. (Electro)catalytic processes discussed in this review include, water oxidation, methanol and carbon dioxide reductions. Bulk nanoporous structures made by selective leaching can be used either directly as high-performance (electro)catalysts, or indirectly as 3D bulk current collectors along with poorly conducting (electro)catalyst materials, achieving greatly enhanced catalytic performance in both situations. While traditional 2D thin film water oxidation electrocatalysts perform very well in the thin film format (a few nanometers thickness), the absence of robustness in these films restricts their use in practical devices such as water electrolyzers.

Bulk nanoporous materials seem to be the best solution as they combine the robustness of macroscale materials with the remarkable (electro)catalytic properties of nanoscale structures. In fact, several recent reports have demonstrated the high performance dealloyed bulk nanoporous NiFe-based systems as water oxidation electrocatalysts. Some drawbacks of nanoporous heterogeneous electrocatalysts are highlighted, including the material costs in the case of noble metals, and the long-term stability associated with coarsening during electrocatalytic processes.

Along these lines of developments nanoporous metals can be used both as template and as catalyst. Recently a solid-state-growth approach for the synthesis of 3D interconnected bicontinuous nanoporous graphene with the aid of nanoporous Ni templates was designed [138], but importantly at low temperatures (600–800 °C) representing the actual novelty. It was shown that the pore size can be tuned through the low-temperature solid-state-growth method and in fact the nanoporous Ni template plays a double role, both as nanoporous template and as catalyst for graphene growth. Besides in energy storage, porous graphene is also examined for application in batteries [139]. Interestingly the size of tubular pores could be tailored from tens of nanometers to hundreds of nanometers by adjusting the nanoporous Ni templates and the work provides in our view a competitive strategy for large-scale manufacturing of nanoporous graphene and for design of electrochemical energy storage devices.

Moving forward, the performance of dealloyed 3D nanoporous catalyst materials can further be improved through structural design. Here we believe that the ultimate architecture for this type of applications should involve hierarchical porous structures, where the big porous structures will account for mass transfer in/out the bulk of the material, while the small pore structures provide a large internal surface area for the catalytic reaction. Another way to effectively take advantage of nanoporous architectures in (electro)catalysis is by building upon previous work in the field. Indeed, after several decades of research in the field of catalysis, many high-performance (electro)catalysts have been identified. Therefore, since to date roughly any type nanoporous material can be made owing the various new dealloying strategies, it should be possible to make nanoporous architecture of any material identified as high-performance (electro)catalyst.

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