Review

What do we know about the electrochemical stability of high-entropy alloys?

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High-entropy alloys (HEAs) possess unique physical and chemical properties clearly distinguishable from those of traditional alloys, making them promising candidates for various applications, including electrocatalysis. While the electrocatalytic performance of these alloys has been assessed in detail, the electrochemical stability is often assumed to be improved compared with single metals and simple alloys. Such an assumption is rarely supported by theoretical or experimental data and might be misleading for the further successful implementation of HEAs in real devices. In this review, we provide a brief overview of the current state of this research direction, identify the common pitfalls in assessing alloy stability, and discuss the need for advanced coupled experimental/computational studies directed toward understanding the partial dissolution of elements from alloys.

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Introduction

The production, conversion, and storage of green energy have gained significant interest in recent years. Concerning energy conversion, electrochemical technologies provide numerous solutions to convert electrical energy into energy stored in chemical bonds, including hydrogen production and direct synthesis of other value-added chemicals [1,2]. Single metals such as Pt, Ir, Cu, and Ni or their oxides are the state-of-the-art catalysts in reactions taking place in electrochemical devices. Often, however, single metal catalysts cannot provide sufficient performance, as either the activity, surface reactivity, or stability deteriorates over the reaction time. Mixing elements and forming alloys is one of the oldest strategies to create new materials with advanced physico-chemical and catalytic characteristics, such as hardness, strength, reactivity, and resistance to corrosion. Numerous bimetallic and trimetallic alloys have been developed and tested as catalysts, many of which exhibited advanced performance in catalyzing electrochemical reactions [3].

Combining two or more elements increases the variety of possible surface compositions, allowing for broader research and design of functional materials [1]. Additionally, altered surfaces and structures can lead to improved electrochemical activity, resistance to poisoning, and stability of the alloys [3]. A good example here is PtRu alloy, which is known as a catalyst for alcohol oxidation. PtRu exhibits high activity and resistance to surface poisoning due to its bifunctional character (or synergistic effect), where Pt is responsible for the dehydrogenation of the alcohols, while Ru prevents the surface of the alloy from poisoning [4,5]. Moreover, the alloying helps to lower the consumption of scarce and expensive metals and thus reduces the costs of the catalysts, which is one of the obstacles in the proton exchange membrane water electrolyzers, as Ir catalysts are utilized at the anodes [6].

Following the idea of creating multimetallic compounds and overcoming the limitations of bimetallic and trimetallic alloys, a new class of alloys was invented around 20 years ago [1]. High-entropy alloys (HEAs) consist of at least five elements in near-equiatomic concentrations (5–35 at.%). The scientific community suggested another definition based purely on the value of the entropy of mixing — for HEAs, this value should be higher than $1.5R$, where R is the gas constant [7,8]. In theory, alloying more and more elements together should increase the configurational entropy of mixing, suppressing the formation of the intermetallic phases and possibly stabilizing the solid solution phase. As a class of materials, HEAs have attracted the attention of many research

Figure 1
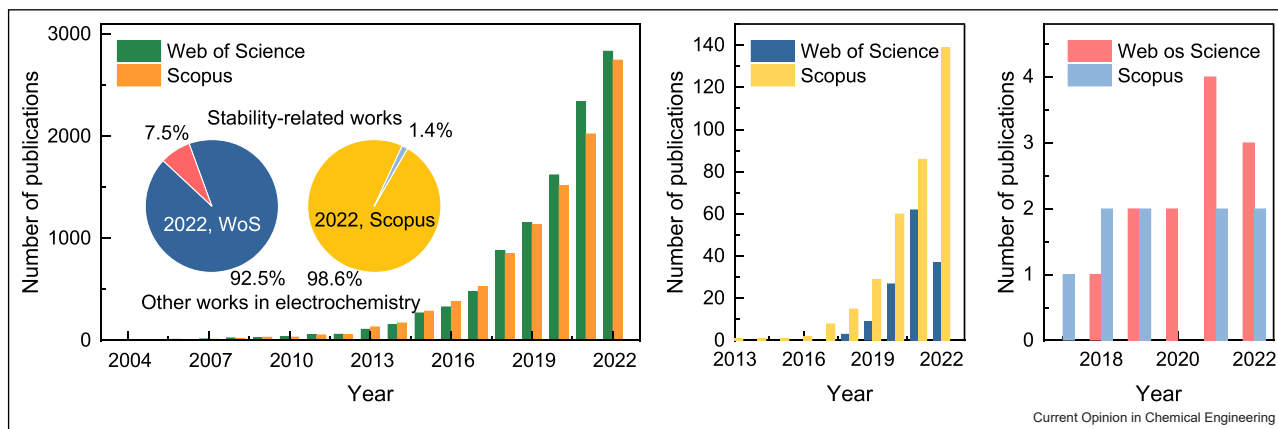
Total number of publications on the topic 'high-entropy alloys' (left), number of publications in the subtopic 'electrochemistry' (middle), and the number of publications about HEAs and electrochemistry with words 'stab(-ility/-ilizing/-le)' in the title (right) depending on the year of publication. The pie charts on the left represent the percentage of stability-related research the total published electrochemical studies of HEAs in 2022. The source of data: Web of Science www.webofscience.com and Scopus www.scopus.com.

groups and have become one of the current hot topics. Figure 1 (left) demonstrates the number of papers published on HEAs every year since their discovery in 2004. Continuously growing interest can also be seen when HEAs are applied as electrocatalysts (Figure 1, middle), although the number of publications is 20 times lower than the total. We expect the interest in HEAs as electrocatalysts to grow even more in the coming years.

In the past couple of years, several applications have been found for HEAs in electrocatalysis [1,2,9]. Mostly metal alloy high-entropy materials were synthesized before the explosion of the research field [10]. Since then, the concept has been extended, and several other types of high-entropy systems were prepared, such as nanostructured HEAs (nanoparticles, hollow nanoparticles, nanowires, nanoplates, etc.) [11–13], high-entropy oxides, sulfides, phosphides, and halogenides [9,10,14,15]. Some HEAs consist of solely noble or non-noble metals and mixed noble-non-noble materials, too. The claimed purpose of the latter is either to decrease the fraction of noble metal(s) in the alloy or to act as a precatalyst, which can be transformed into its active form through a series of activation steps (higher electrochemically active surface area, improved active sites) [16,17].

HEAs have proven to be active electrocatalysts in, for example, hydrogen evolution reaction [18], oxygen reduction reaction (ORR) [17,19,20], carbon dioxide reduction reaction [21], and nitrogen reduction reaction [22]. Besides reduction processes, HEAs can also catalyze the oxygen evolution reaction (OER) [11,16,23] and the oxidation of small organic molecules, such as alcohol oxidation reactions [24,25]. Their high activity is rooted

in their unique surface compositions — due to the random arrangement of metal elements in the alloy structure, leading to the formation of a plethora of various active sites [9]. Moreover, the different atom sizes induce lattice distortions and strain effects, influencing local electronic properties. In return, the latter tailors the adsorption energies of the active sites toward given reactants/intermediates/products, leading to the break of scaling relations and systems with significantly improved electrocatalytic activity [14]. In addition to dark electrocatalysis, the HEA concept has already been extended to photocatalysis [26] and photoelectrocatalysis (e.g. CO_2 reduction) [27].

One aspect rarely addressed in publications (see Figure 1, right) is the electrochemical stability of HEAs. It is understandable that in the current, relatively early stage of HEA electrocatalysis, most studies focus on reporting the highest possible activity and pay little to no attention to long-term stability. Ironically, however, the scientific community gradually realized that in some reactions, materials showing the highest electrocatalytic activity suffer from the most significant stability issues [28]. Hence, proper stability assessment must be done even in performance-oriented studies. The stability of HEAs almost exclusively has been characterized using *ex situ* techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction analysis (XRD), and scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) [16,23,29]. While electrolyte post-analysis has become a common practice in electrocatalysis research, there are almost no studies in the literature where the electrolyte was carefully analyzed to identify any metal ions leached from the HEA structure after a long-term experiment.

However, learning from the recent developments stressing the importance of fundamental studies on electrocatalyst stability [30,31], we anticipate growing research interest in this area and a need for a brief literature analysis, which is presented below.

Dissolution of single metals and simple alloys

Initial guesses about the tendencies of single metals toward dissolution can be made based on thermodynamics, according to Pourbaix diagrams. However, these predictions do not consider the influence of kinetics. Without rigid theoretical models describing metals and alloy dissolution during electrocatalytic applications, stability descriptors for some single metals were proposed based on *in situ* dissolution measurements [30,32,33]. However, while exploring the dissolution of the bimetallic systems, it became clear that introducing just one additional metal to the catalyst already makes it much more difficult to explain the dissolution processes during electrochemical reactions [34]. Moreover, mixing many elements together to achieve a high-entropy effect does not guarantee the formation of a single-phase solid solution, as the literature shows, which just adds to the complexity [35,36]. Hence, before focusing on the stability of HEAs, we briefly discuss the dissolution behavior of simple bimetallic alloys.

Concerning the electrocatalytic applications of alloys, dissolution may or may not play a destructive role. To understand whether catalyst dissolution is detrimental to a given application, we first need to answer a critical electrocatalysis question, "Do all elements need to be present on the catalyst's surface for it to be stable and functional?" To elaborate more on this question, we identify and discuss several scenarios related to alloyed elements' *bifunctional* versus *electronic* functions in catalysts.

A good illustration of the bifunctional mechanism is PtRu alloy, which is mentioned above. It is anticipated that both metals must be present on the surface since Pt and Ru sites provide different functionalities, that is, dehydrogenation and surface depoisoning. Concerning electrochemical stability, although Pt stabilizes Ru, shifting its onset potential of dissolution to higher values than predicted by thermodynamics and measured for the single Ru metal, the leaching of Ru still occurs at a much higher pace than Pt, leading to the Pt enrichment of the surface and disappearance of Pt–Ru bifunctional active sites. The complete dissolution of Ru from the alloy's surface makes the alloy perform as pure Pt, highlighting the crucial role of the Pt–Ru surface sites [3,4]. Another example of such a bifunctional effect is the PdAu electrochemical H_2O_2 production electrocatalyst, where preferential dissolution of Pd results in Au surface enrichment and ORR overpotential increase to the values

observed for pure Au [37]. These works demonstrate how dealloying and leaching of one element can lead to the loss of the alloys' catalytic functionality.

Unlike the bifunctional mechanism, electronic effects could still play a role even when one of the elements is fully leached from the surface. Severe leaching of less stable elements from the surface of the alloy and formation of a core-shell structure in Pt-M alloys (where M is non-noble metal, e.g. Cu, Ni, or Co) have been demonstrated in many studies [34,38,39]. Such alloys have broad applications in fuel cells, where the ORR activity of Pt catalysts can be improved by the alloyed core, which exhibits properties different from the Pt-enriched surface. Several factors should be considered. The shell of the more stable Pt prevents further dissolution of less noble components, resulting in overall catalyst stability and long-term functionality at lowered Pt loading and cost. At the same time, the shell exhibits compressive lattice strains caused by the presence of relatively small transition metals in the core, weakening ORR intermediates adsorption strength [34,38,39]. While theoretical studies also predict improved Pt stability due to weakened Pt-O bond strength [40], this prediction was not yet demonstrated experimentally probably because the effect is masked by severe non-noble element leaching [41,42].

Independent of the alloy functionality mode, selective metal leaching, if well controlled, offers countless opportunities to tune the *precatalyst* surface composition and, thus, the electrocatalytic properties of the materials [37]. It is, however, challenging to prepare the catalyst surface of the highest activity during synthesis and maintain it during the operation. As a representative example, a purposefully synthesized $PtCu_3$ core-shell ORR catalyst can be considered. It was shown that it has significantly lower ORR activity than $PtCu_3$ dealloyed *in situ* [34]. The stability of bimetallic alloys may be tuned further by adding extra elements. Thus, decorating the surface of $PtCu_3$ alloy with low amounts of Au hinders the dissolution of both Pt and Cu and decreases carbon corrosion in the support [43].

The above examples demonstrate that controlling the surface and near-surface composition of as-synthesized and operational catalysts is essential for their functionality, especially when the bifunctional mechanism is operative. This fact implies a pressing need for precise surface structure analysis, elemental distribution, and compositional/structural changes during the operation. Unfortunately, when it comes to actual operational conditions, the composition and arrangement of different metals at the electrocatalyst surface rarely match the nominal or bulk composition, and surface dynamics is difficult to predict. Moreover, already during the synthesis and storage in air, surface segregation processes are likely to occur. Again,

taking PtRu as a representative model system, Ru is a more oxophilic element than Pt [44], so, under an oxygen atmosphere or in air, it tends to migrate from the bulk to the electrocatalyst surface, enriching it in Ru (see below). Such processes are rarely studied and discussed in the literature but may result in misleading conclusions, for example, when nominal surface compositions are erroneously considered in density functional theory calculations. While the need for knowledge and control of surface composition is undisputable, modern surface science analysis tools are limited in providing this information. XPS and X-ray absorption spectroscopy are standard workhorses in synthesis and material science research, as well as in studying HEAs [19]. However, neither provides a monolayer surface composition resolution for applied nanoparticulated catalysts. Atom probe tomography and low-energy ion scattering are more surface sensitive than XPS but are rarely used for such complex compounds [45,46]. (Scanning) transmission electron microscopy can also be valuable complementary tools in visualizing the morphology and homogeneity of the HEA nanoparticles. However, the latter has to be handled with care (and complemented with data provided by other techniques). Electrochemical methods demonstrate good surface sensitivity and can provide meaningful insights about catalyst changes during the operation but are currently applicable only to a few alloys, for example, PtRu [47].
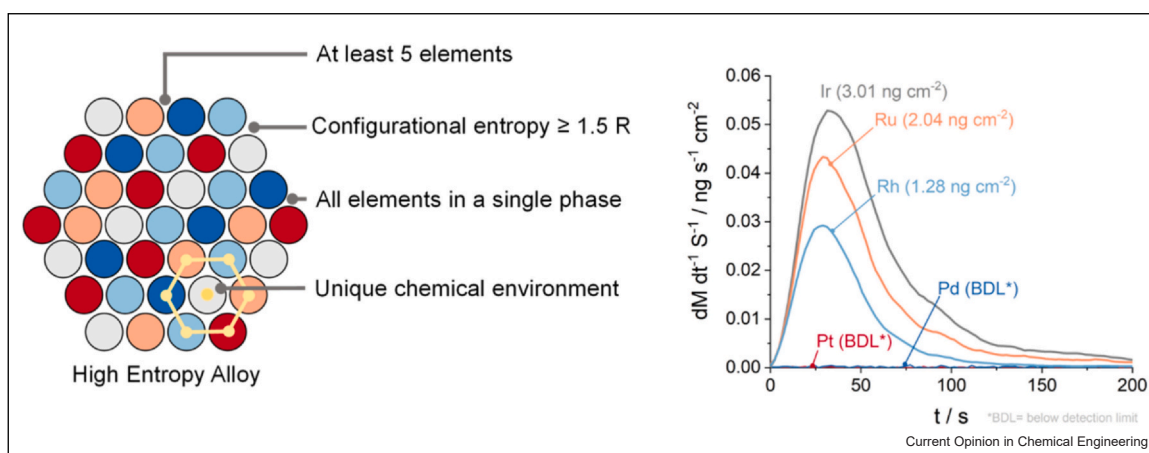
Dissolution of high-entropy alloys

HEAs have already demonstrated their high potential in applications where bulk material properties are the most important (e.g. strength, ductility) [48,49]. HEAs proved to be very stable in these application scenarios, and their

success in these neighboring fields stimulated the electrocatalysis research community to test these materials in chase of significantly improved performance. However, as was stressed before, requirements for electrocatalysts are considerably different. Here, the surface and near-surface regions are the most important (which atoms are present, composition, arrangement, the effect of bulk on surface properties, etc.) [50]. Therefore, it is of utmost importance to precisely determine the surface composition of HEAs and the exact chemical state of the surface atoms. Are there all alloy constituents at the catalyst surface and in a similar amount as in the bulk? As was outlined in the previous section, answering this question is rather challenging even for bimetallic alloys, but the parameter space in the case of HEAs is considerably bigger (at least five elements instead of two), where the physicochemical properties of each constituent must be considered [9]. For example, even with tedious synthesis and handling of samples, a thin layer of native oxides forms at the electrocatalyst surface when it comes into contact with air [32]. Whenever the electrocatalysts are placed in the electrolyte and potential is applied, this native oxide layer is reduced, leading to a transient dissolution of alloy constituents [32], irreversibly altering the surface composition of the HEA. An example of the phenomenon is presented in Figure 2.

Interestingly, no dissolved Pt and Pd were detected, even though these metals also tend to form native oxides that cathodically dissolve [32]. This means that either other metals and the alloy structure stabilized Pt and Pd in their metallic state or only Ru, Ir, and Rh were present at the catalyst surface due to their considerably

Figure 2

Simplified 2D representation of a HEA nanoparticle showcasing its main properties (left). Contact peaks recorded for an equimolar PtRuIrRhPd high-entropy alloy in 0.1 M $HClO_4$ electrolyte (right). Metal dissolution occurred when the electrolyte came in contact with the working electrode (i.e. the HEA sample) under potential control (E = +0.05 V_{RHE}). The amount of dissolved metal is indicated in the parentheses, which was obtained by integrating the contact peak feature for each metal. Contact dissolution was below the detection limit (BDL) for Pt and Pd. The rest of the dataset is published in our recent work [51].

Figure 3
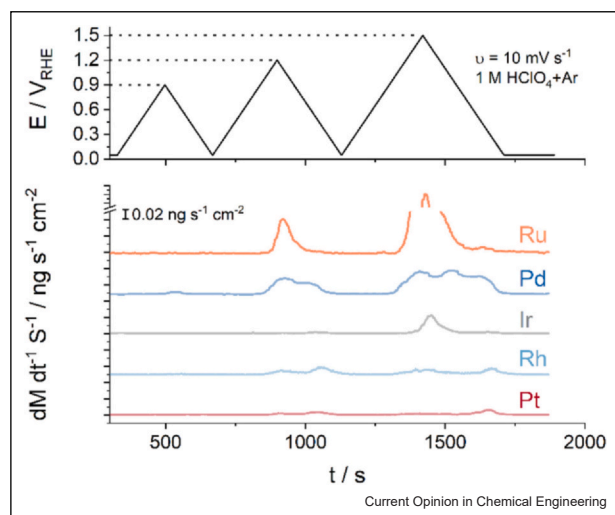
Dissolution profiles recorded for a sputtered PtRuIrRhPd (equiatomic composition) HEA thin film. Measurements were performed in 0.1 M HClO$_4$ electrolyte, applying a 10 mV s^{-1} scan rate. The protocol consisted of three cyclic voltammograms with gradually ($\Delta E = 0.3$ V) increasing the upper potential limit. The potential profile is presented above the dissolution data. The contact peak area was removed for clarity. If needed, the recorded dataset was smoothed using a fast Fourier transform (FFT) filter (points of window = 5–8). More information on the samples can be found in our recent paper [51].

higher oxophilicity [44]. The presented data show that the number of metal ions dissolved during the reaction can be effectively quantified in real time using, for example, online inductively coupled plasma mass spectrometry (ICP-MS) [51], but the collected data tell nothing about the configuration of atoms at the electrocatalyst surface along with their chemical state. This effect is almost always neglected (but it inevitably happens for all electrocatalysts stored under ambient conditions), and calculations are based only on the nominal or surface composition determined before the *ex situ* electrochemical measurements. How safe is it to assume that the specific combination of a minimum of five elements provides unique active sites and coordination environment if the exact surface composition is unknown during the reaction?

Recently, we attempted to quantify the degradation of various noble metal-based multimetallic alloys, including HEAs, using online ICP-MS [51]. To illustrate this, a set of dissolution curves (dissolution rate vs time) is presented in Figure 3, recorded for a PtRuIrRhPd (equimolar composition) HEA sample in 0.1 M HClO$_4$. The main lesson that we have learned is that it is immensely complex even to carry out such measurements, starting from designing the electrochemical protocol itself (e.g. considering the thermodynamic stability

window of each element), carefully selecting the internal standards, the isotopes that have to be tracked by the ICP-MS and to identify all interfering ionic species. Overall, these are considerably easier for monometallic/simple alloys. We concluded that, in order to extract meaningful information for further application in actual devices, the stability of HEA electrocatalysts should be assessed only if they are tested under conditions (protocol, electrolyte, pH, etc.) mimicking those typically present in electrocatalytic experiments [51].

To the best of our knowledge, HEAs are almost exclusively tested in fundamental electrochemical setups (small area three-electrode cells or model electrolyzers). This is rooted in the peculiarity of the state-of-the-art synthesis methods of HEAs [2,9,10,12,52,53], which are often not possible to be scaled up. Because of this, there are only a few attempts in the literature (examples are mostly in the battery and fuel cell communities) to test these promising electrocatalysts in real devices [11,20,24]. Therefore, the assumption that observations/trends regarding the activity, selectivity, and stability of HEAs can be directly transferred to real devices must be taken with a grain of salt. Operating conditions are far from equilibrium (high current densities, pressure, temperature, etc.). For example, Ru-based catalysts are proven to be the most active in the OER. However, the high activity is associated with significant leaching of Ru from the crystal lattice thanks to the lattice oxygen oxidation mechanism and RuO$_4$ formation [28]. This degradation pathway can be significantly more pronounced if the electrolyzer cell is run under industrially relevant conditions. Thus, to make valid conclusions, the community needs to move away from model systems and test promising HEA electrocatalyst candidates under industrially relevant conditions.

Conclusions and outlook

HEAs have shown superior activity and selectivity in a wide range of electrocatalytic reactions. The assumption regarding their outstanding stability in these originates from either theory (purely thermodynamic standpoint) or long-term electrochemical measurements followed by *ex situ* materials characterization. However, it can be firmly stated that the field is in its infancy; there is no unified theory that can precisely describe/model the degradation of these complex materials. A very limited amount of experimental data regarding the stability of these materials has been published so far, and it can be concluded that the methods (only electrochemical protocols and *ex situ* tools) are not enough. It also must be noted that HEAs have almost exclusively been tested in fundamental electrochemical setups and not in real devices. Among other performance metrics, stability can be drastically different.

All in all, the above-described limitations clearly mark the path for future HEA-related research campaigns:

- Stability should be tested under conditions typically occurring in electrocatalytic reactions (electrolyte, pH, potential window). Purely electrochemical methods and *ex situ* characterization tools are insufficient since they provide very little information on the development of the electrocatalyst surface. *In situ* techniques will pose a possible solution and, for example, online ICP-MS will play a pivotal role [51] in the future in the assessment of HEA stability in parallel with techniques that can rapidly measure the surface composition and the oxidation state of each constituent under process conditions.

- The parameter space is several magnitudes bigger compared to simple metals/alloys due to the number of alloy constituents (at least five). There is an inevitable need to optimize the number/length of experiments. Applying autonomous workflows with machine learning tools should play a dominant role in tackling these challenges [54,55].

- Published research results regarding the activity/selectivity/stability of HEAs were almost exclusively measured using model systems and laboratory scale setups. Promising electrocatalyst candidates should be tested in real devices under industrially relevant conditions (electrolyte, pH, temperature, pressure, etc.). These efforts should involve the development of advanced synthesis routes [52], allowing the scale-up of HEAs production.

- Finally, in parallel with the development of experimental tools, theoretical models have to be refined [50]. These two approaches should go hand in hand to uncover and fully understand the degradation behavior of HEAs.

Data Availability

Data will be made available on request.

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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