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Good Practice Report

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Interpretation of galvanic series when teaching metal corrosion

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Abstract: The article discusses the knowledge of students in metal corrosion. Usually, resistance of metals against corrosion is determined by the values of the standard electromotive force (EMF) of the metals determined versus the standard hydrogen electrode (SHE). However, the standard conditions differ from the real-world conditions under which metal corrosion occurs, so the standard EMF cannot be accepted as an absolute indication of metal`s resistance to corrosion. This difference is due to many environmental factors (e.g., temperature, pH, pressure, concentrations of hydrogen and oxygen in the environment etc.); thus, the value of metal potential is affected. Therefore, the authors have suggested using stationary (corrosion) potentials of metals and galvanic series instead of the standard EMF in the education process. In the article, the authors present a comparison of metal activity series based on standard EMF and galvanic series. The advantage of the galvanic series offered to students studying corrosion is illustrated by the problematic tasks for light metals (Ti, Mg, and Al) and corrosion galvanic cells. Based on the presented values of the metal potentials in the galvanic series, students were able to correctly choose the type of metal coating, they can calculate the EMF values of the corrosion process more accurate and verify them experimentally during the laboratory session.

Keywords: standard electromotive force; stationary potential; galvanic series; light metals; corrosion

1 Introduction

Corrosion of metals is an important issue related to the use of metals in industry, and it impacts the economy and ecology of any country. The cost of corrosion worldwide was estimated to be $2.5 trillion, which was equivalent to 3.4 % of the 2013 global Gross Domestic Product (GDP).[1,2] In developed countries, 25 % of the metals produced corrode every year, of which 10–15 % corrode irreversibly and cause up to 276 billion dollars damage only in the United States annually.[3]

Great attention has been paid to corrosion of metals, especially iron or steel,[4–9] in the education process. It has been observed that 20 % of the iron and steel produced annually is used to replace rusted metal.[10] Therefore, the control and prediction of corrosion are of paramount importance. Metal corrosion is one of the most difficult parts of chemistry for students and one of the greatest challenges in engineering education.[11,12]

Most students who studied chemical engineering, mechanical engineering, and textile industry, graduated from the university, and work in equipment design, have demonstrated a significant lack of understanding of corrosion processes. Most first-year bachelor`s students (18–19 years old) have studied chemistry only up to the 10th grade in school, where minimal attention was given to the topic of corrosion. In university bachelor`s studies, only 4–5 out of 32 h of general chemistry taught during one (usually the first one) semester are dedicated to corrosion. In both school and university settings, the reactivity and corrosion resistance of the metals are typically

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evaluated based on the values of the standard electromotive force (EMF) or the electrode potentials of the metals determined versus standard hydrogen electrode (SHE) under the following unchanging conditions:[13] a temperature 25.00 °C, an effective concentration of 1 mol/L and a partial pressure 100 kPa (1 bar). The reactivity of metals is associated with EMF in many modern textbooks.[10,14,15]

However, this raises a question, is standard EMF a valid tool for interpreting metal corrosion in real-life?

It is important to note, that the metal activity series based on standard EMF is an oversimplification; thus, it cannot be accepted as an absolute indication of resistance of metals against corrosion and does not reflect the behavior of real metals in practice. In fact, some metals, such as iron and stainless steel, often react with the hydrogen ions present in the aqueous solvent, resulting in a significant difference in the potential values of metals as they become covered with a thin film of oxides. For example, 316 stainless steel is passive (does not corrode) at the potential −0.1 V versus standard calomel electrode (SCE) because it is protected by a thin oxide film, while it corrodes at the potential −0.4 V versus SCE.[16]

Therefore, the behavior of metals and, at the same time, their stationary or corrosion potentials depend on both internal factors associated with the nature of the metal and external factors associated with the composition of the electrolyte and physical conditions. Internal factors include: the physical and chemical state, phase[17] and structure of the metal, the state of the surface, the presence of mechanical deformations and stresses[18] etc. External factors depend on the corrosion environment: the chemical nature of solvent, the concentration of hydrogen and the amount of oxygen in the environment,[6,19–21] temperature,[6,22,23] pressure, the mixing of the solution and solution flow rate,[24] the solution pH,[6,21] the presence of Cl^- in electrolyte[25] and the ability of Cl^- to locally dissolve in the thin passive metal oxide layer,[26–28] etc. It has been observed that at the initial stage of corrosion the importance of "corrosion environment" is more than 80 %.[29] Climate change alters the corrosive behavior of the environment and increases the risk of corrosion failures.[30]

Due to the influence of all these parameters, the use of galvanic series is suggested to better understand the corrosion and predict early metal corrosion. The galvanic series of metals is organized according to the numerical values of their stationary potentials, which are determined only empirically in seawater or in neutral medium (3–3.5 % or 0.1 M NaCl; concentration of NaCl is associated with concentration of NaCl in salt fog chamber).[31] The seawater galvanic series is used to predict the effects of the corrosion in other environments for which no data is available. The average stationary potential values based on the literature analysis are provided in the table and no metal alloys have been used (Table 1).

To address this, we decided to explain to students the difference between the standard EMF and the galvanic series, which could help them better understand the real-world compatibility of metals and enhance their ability to design various machine components under practical conditions.

Table 1: Corrosion potentials of some commonly used metals in practice (versus SHE) compared with their standard EMF.

Standard EMF	E^0, V	Galvanic series	E_{corr}, V
Mg	−2.363	Mg	−1.480
Al	−1.663	Mn	−1.000
Ti	−1.630	Zn	−0.880
Mn	−1.179	Al	−0.530
Zn	−0.763	Cd	−0.500
Cr	−0.744	Fe	−0.420
Fe	−0.440	Pb	−0.310
Cd	−0.403	Sn	−0.210
Ni	−0.250	Cr	−0.080
Sn	−0.136	Ni	−0.010
Pb	−0.126	Cu	+0.060
Cu	+0.337	Ti	+0.100
Ag	+0.799	Ag	+0.230
Au	+1.498	Au	+0.250

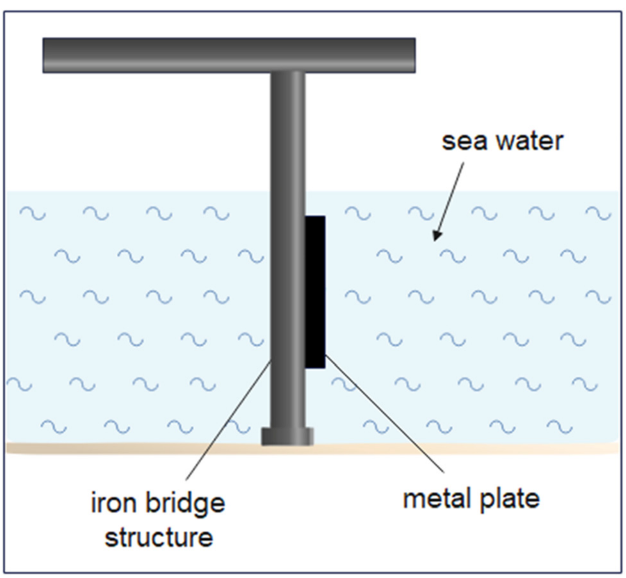
2 Research objective and methodology

The aim of this research was to introduce students to stationary potential and to investigate the ability of the first-year students to understand the difference between standard EMF and galvanic series while learning about metal corrosion.

This research was conducted during the 2018/2019 and 2019/2020 academic years, with 36 first year students participating each year. The students were tested during the teaching of the topic "Corrosion of metal" in the "Chemistry" module, without considering gender distribution. In the 2018/2019 academic year, students were introduced only to the standard EMF, while in 2019/2020, they were introduced to both the standard EMF and the galvanic series. To assess how well students understood the material presented in lectures, they were given a questionnaire consisting of five questions:

1st task

The picture shows a bridge structure with a part submerged in sea water. In this picture, the iron structure is protected from corrosion by a plate of another metal attached to it. Using EMF series, provide an example of a metal for:
A – a plate made of which would protect an iron structure from corrosion;
B – an example of a metal that, when used as a plate, protects this structure from corrosion.



A answer – ……………………………………………….
B answer – ……………………………………………….

2nd task

Ti, Al, and Mg are highly reactive metals, yet they are extensively used in various industries, including automotive, aviation, and space technologies. Explain why, despite their high reactivity, Ti, Al and Mg, along with their alloys, are widely used in practice.
C answer – ……………………………………

3rd **task**

Choose an anodic coating for manganese protection from corrosion in neutral medium.
D answer…………………………………….

4th **task**

Zinc-plated aluminum is in aqueous solution and the zinc coating is scratched. Is zinc coating anodic or cathodic? Calculate electromotive force. Write half reactions of anodic and cathodic processes and draw a corrosion scheme based on the corrosion algorithm.[32]
E answer……………………………………

5th **task**
Calculate EMF of corrosive galvanic cell and verify it with an experimental value measured with a laboratory experiment.
F answer………………………………….

Each correct answer was scored with one point (maximum number of points 5), and the duration of the test carried out in the laboratory was 60 min. This included 30 min for conducting an experiment to measure the EMF of corrosion galvanic cells.

3 Results and discussion

Table 2 presents the responses of the students who participated in the study using the standard EMF during 2017/2018 and both the standard EMF and the galvanic series during 2018/2019.

As shown in Table 2, in the 2018/2019 academic year, when students relied on the standard EMF values commonly used in Lithuanian schools and universities (Table 1), they made two key errors. Firstly, in seawater, the potential of Ti and Cr increase significantly (see Table 3), meaning Ti and Cr would not protect the iron support of the bridge. Secondly, although the standard EMF of cadmium is 37 mV higher than that of Fe (Table 1), the stationary potential of Cd in the given medium (seawater) is 80 mV lower (Table 1) than that of

Table 2: Student responses options and student numbers.

Student answers options	Number of students	
	2018/2019	2019/2020
A		
The symbol of one of the metals of I-II groups	9	0
The symbol of one of the metals on the left (except metals of I-II groups) from Fe in the metal activity series based on standard EMF	27	5
The symbol of one of the metals on the left from Fe in galvanic series	0	31
B		
The symbol of one of the metals to the right of Fe in the metal activity series based on standard EMF	36	5
The symbol of one of the metals to the right of Fe in galvanic series	0	31
C		
No answer	13	0
Light metals with varnish-paint coatings or using inhibitors can temporarily protect light metals from corrosion	23	8
The possibility of light metals practical use because a huge increase in the potential values of light metals	0	28
D		
Anodic coating: Ti or Al	26	4
Anodic coating: Mg	10	32
E		
Zn is **cathodic** coating, corrode aluminum	36	4
Zn is **anodic** coating, corrode zinc	0	32
F		
A small overlap of the calculated EMF value and verified EMF determined experimentally in the laboratory	36	3
A large overlap of the calculated EMF value and verified EMF determined experimentally in the laboratory	0	33

Table 3: Change the potential values of metals.

Metal	E^0, V	E_{corr}, V	$\pm\Delta E = E_{corr} - E^0$, V
Mg	−2.363	−1.480	0.883
Al	−1.663	−0.530	1.133
Ti	−1.630	+0.100	1.730
Cr	−0.744	−0.080	0.664
Zn	−0.763	−0.880	−0.117
Mn	−1.179	−1.000	0.119
Fe	−0.440	−0.420	0.020
Cd	−0.403	−0.500	−0.097
Ni	−0.250	−0.010	0.240
Sn	−0.136	−0.210	−0.074
Pb	−0.126	−0.310	−0.184
Cu	+0.337	+0.060	−0.277
Ag	+0.799	+0.230	−0.569
Au	+1.498	+0.250	−1.248

Fe according to the galvanic series. Therefore, in the given medium (seawater), Cd would protect Fe from corrosion.

When answering C during the 2018/2019 academic year, students who used only metal activity series based on the standard EMF found it challenging and could not explain why light metals (Ti, Al and Mg) are widely used in practice. A few students presumed that light metals with varnish-paint coatings or using inhibitors can temporarily protect them from corrosion, allowing short-term practical use. Interestingly, the seemingly simple answer of the second task C was critical stumbling block. In the 2018/2019 academic year, no student achieved the maximum score of five points. However, in the 2019/2020 academic year, when students used both the standard EMF and the galvanic series (Table 1), they observed a significant increase in the potential values of Ti, Al and Mg (Table 3) and understood the practical applications of these light metal. In contrast, for the 2019/2020 academic year stuents, answer C to the second task did not cause difficulties and did not prevent them from scoring the maximum number of points.

Summarizing the changes in the potentials values of metals presented in Table 3, students observed that, under real conditions, the potential values of metals increased by approximately 50 % of the cases (seven cases out of fourteen).

From the given examples of the students' solutions for tasks 3 and 4 (answers D and E in Table 4), it is evident that relying solely on standard EMF led to incorrect conclusions, which were corrected with the help of the galvanic series.

Students could verify their EMF calculations (Table 4, answer F) by experimentally measuring the EMF of corrosion galvanic cells (Table 5 and Figure 1). E_{exp} values were determined as the average of three measurements. In most cases, the E values calculated using potentials of metals from galvanic series showed good correlation with values of E_{exp}.

It is important to note that E_{exp} values measured by the students correlates well with the EMF values reported in literature.[34]

Following the research, we decided to introduce the comparison of metal activity based on standard EMF and galvanic series (Figure 2) to students studying metal corrosion in the next academic year.

Table 4: An example of a student solution for Tasks 4 and 5.

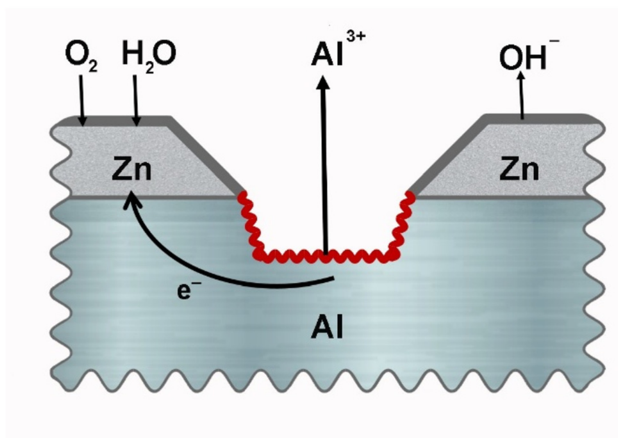
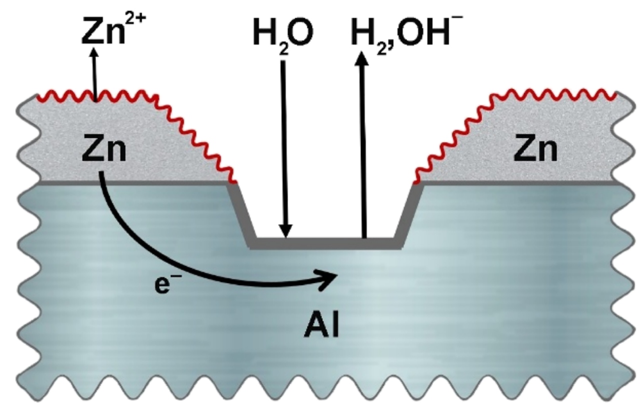
Answer	Standard EMF (2018/2019)	Galvanic series (2019/2020)
E	$E^0(Al^{3+}/Al) = -1.663$ V; $E^0(Zn^{2+}/Zn) = -0.763$ V Conclusion: Zn is **cathodic** coating, corroding aluminum. Calculation of EMF:[33] $E^0 = E^0{}_{cathode} - E^0{}_{anode}$ $E^0 = E^0(Zn^{2+}/Zn) - E^0(Al^{3+}/Al) =$ $= -0.763$ V $- (-1.663$ V$) = 0.90$ V Half equations of anodic and cathodic processes: A (Al): $Al^0(s) \rightarrow Al^{3+}(aq) + 3e^-$ C (Zn): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ Corrosion scheme:  The reaction of the corrosion process: $4Al(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al^{3+}(aq) + 12OH^-(aq)$ $4Al(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al(OH)_3(s)$	E_{corr} (Al) = -0.530 V; E_{corr} (Zn) = -0.880 V Conclusion: Zn is **an anodic** coating, corroding zinc. Calculation of EMF: $E = E_{corr}$ (Al) $- E_{corr}$ (Zn) = $= -0.530$ V$- (-0.880$ V$) = 0.35$ V Half equations of anodic and cathodic processes: A (Zn): $Zn^0(s) \rightarrow Zn^{2+}(aq) + 2e^-$ C (Al): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ Corrosion scheme:  The reaction of the corrosion process: $Zn(s) + 2H_2O(l) \rightarrow Zn^{2+}(aq) + H_2(g) + 2OH^-(aq)$ $Zn(s) + 2H_2O(l) \rightarrow Zn(OH)_2(s) + H_2(g)$
F	$E^0(Al^{3+}/Al) = -1.663$ V; $E^0(Cu^{2+}/Cu) = 0.337$ V Calculation of EMF:[33] $E^0 = E^0{}_{cathode} - E^0{}_{anode}$ $E^0 = E^0(Cu^{2+}/Cu) - E^0(Al^{3+}/Al) = = 0.337$ V $- (-1.663$ V$) =$ **2.00 V**	E_{corr} (Al) = -0.530 V; E_{corr} (Cu) = = 0.100 V Calculation of EMF: $E = E_{corr}(Cu) - E_{corr}(Al) = 0.100$ V $- (-0.530$ V$) =$ **0.63 V**
	Students experimentally determined that EMF of Al–Cu corrosive galvanic cell was 0.66 ± 0.02 V depending on the accuracy of the experiment (see Table 5).	

Table 5: Comparison of standard EMF, EMF calculated using galvanic series and experimental EMF of some corrosion galvanic cells M_1 |NaCl(aq)| M_2.

Galvanic cell	Standard EMF $E^0 = E^0_{cathode} - E^0_{anode}$, V	Galvanic series $E = E_{corr}(M_1) - E_{corr}(M_2)$, V	E_{exp}, V measured in 0.1 M NaCl
Al–Cu	2.000	0.63	0.66 ± 0.02
Al–Fe[a]	1.223	0.11	0.21 ± 0.02
Al–Sn	1.527	0.32	0.34 ± 0.03
Sn–Cu	0.473	0.27	0.21 ± 0.02
Fea–Cu	0.777	0.48	0.42 ± 0.03
Mn–Fe[a]	0.739	0.58	0.65 ± 0.02
Mn–Zn	0.416	0.12	0.21 ± 0.02
Zn–Fe[a]	0.323	0.46	0.41 ± 0.03
Zn–Cu	1.100	0.94	0.88 ± 0.01
Al–Zn	0.900	0.35	0.30 ± 0.02
Ni–Cu	0.587	0.07	0.13 ± 0.03
Pb–Cu	0.463	0.37	0.41 ± 0.01

[a]Mild carbon steel St-3 (GOST 380-94) is equivalent to steel ASTM 570 grade 36.

Metal	Medium: 0.1 M NaCl
M_I: **Sn**	**E_{corr} = –0.21 V** **~~anode~~/cathode** (leave the correct word)
M_{II}: **Al**	**E_{corr} = –0.53 V** **anode/~~cathode~~** (leave the correct word)
$E = E_{corr}(M_1) - E_{corr}(M_2)$, V	**E = –0.21 V – (–0.53 V) = 0.32 V**
E_{exp} (I = 0), V	**E_{exp} = 0.34 V**
E_{volt} (I ≠ 0), V	**E_{volt} = 0.08 V**
$\Delta E = E_{exp} - E_{volt}$, V	**ΔE = 0.26 V**
Cell diagram	**⊖Al | NaCl(aq) | Sn ⊕**
Equations of electrode processes	**A(Al):** **$Al^0(s) \rightarrow Al^{3+}(aq) + 3e^-$** **C(Sn):** **$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$** **or** **$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$**

Figure 1: An example of the report of students' laboratory session "Galvanic cells".

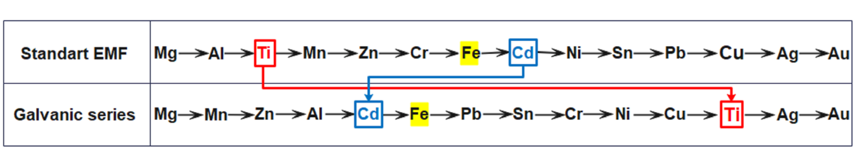


Figure 2: Comparison of metal activity series based on standard EMF and galvanic series.

4 Conclusions

The manuscript presents a comparison of metal activity series based on standard EMF and galvanic series is presented. We demonstrated that using the galvanic series provides significant advantages for students in understanding and solving corrosion problems. The use of galvanic series is advantageous during the design stage, as it allows for the early prediction of metal corrosion in the project. The use of galvanic series for education purposes helps to better understand the real metal corrosion processes and to correctly choose the type of metal coating that enables more accurate calculations of EMF values and allows them to verify with real values. Students observed that under real conditions the potential values of metals increased in approximately 50 % of the cases (seven cases out of fourteen).

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Informed consent: Informed consent was obtained from all individuals included in this study, or their legal guardians or wards.
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Use of Large Language Models, AI and Machine Learning Tools: Not applicable.
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