Method of sacrificial anode transistor-driving in cathodic protection system

M. Narozny, K. Zakowski, K. Darowicki

Department of Electrochemistry, Corrosion and Materials Engineering, Chemical Faculty, Gdansk University of Technology, 11/12 Narutowicza St., 80-233 Gdansk, Poland

a b s t r a c t

A magnesium anode driving system has been proposed. A PNP driving transistor has been used. Electrochemical testing in 3%NaCl, results and comparison of the driving system and classic direct anode to cathode connection are presented. The driving system reduced the protection current and stabilized the working conditions of the anode. Higher anode efficiency was achieved. Overprotection and hydrogen embrittlement threats were prevented and the potential of the cathode met the protection criterion. The expected anode operating time has been prolonged.

Keywords: A. Magnesium B. Polarization B. Weight loss C. Cathodic protection

1. Introduction

Metal constructions are protected against corrosion by protective coatings and cathodic protection. These technologies are complementary. The worse the coating condition is the greater the current demand for cathodic protection is. There are a few methods of providing protection current. The first method utilizes the connection of galvanic anodes to the protected structure [1]. Anodes have to have more negative potential than the protected metal. The other method uses an external direct current source and an impressed current anode [2]. A metal is fully protected against corrosion if it is polarized to a threshold protection potential. In such a case, an anodic reaction occurs on the surface of an electrically connected galvanic anode or an impressed current anode. Virtually only a cathodic reaction takes place on the surface of a protected metal. Complete inhibition of corrosion is possible if a cathodic protection system is well designed and operated.

A quantity of impressed current cathodic protection systems – ICCP is declining. The main reasons are several times higher maintenance costs, inspection and service costs compared to galvanic anode systems [3,4]. In several countries jural acts recommend galvanic anode systems only for protection of offshore oil industry constructions [5].

Sacrificial anodes made of zinc or aluminium with potential against an Ag|AgCl|Seawater reference electrode being equal to −1.05 V and −1.1 V, respectively are most often used in order to provide cathodic protection to marine structures. In their classical application, anodes are welded to the surface of the protected structure. There are also technical solutions in which a groundbed is connected to the structure with a cable [6,7].

Magnesium is also used for galvanic anodes production. It is uncommon to use magnesium sacrificial anodes to protect marine constructions [7]. The main reason for that is a risk of excessive polarization of the protected structure – the overprotection [8,9]. In such a case, water decomposition and hydrogen evolution might take place and cause the coating disbondment phenomenon [10]. Several grades of steel are prone to hydrogen embrittlement and cracking [11]. Thus, the potential of a cathodically protected structures should be kept within the range of −0.8 V to −1.05 V against Ag|AgCl|Seawater reference electrode, which corresponds to +0.25 V to −0.05 V against Zn|Seawater reference electrode [12]. The cause of excessive polarization of steel is a very low standard potential of magnesium (−1.5 V in seawater against Ag|AgCl|Seawater electrode) and very low resistivity of seawater – approximately 0.3 Ωm. These factors affect cathodic protection current intensity I_{pc}, which is described by the following relationship (Eq. (1)):

$$I_{pc} \frac{E_C - E_A}{R} \tag{1}$$

where E_C and E_A is the potentials of the cathode (protected structure) and sacrificial anode, respectively, R is effective resistance of the sum of all resistances in a cathodic protection circuit (cathodic current outflow resistance, electrolyte resistance, construction resistance, electrical connections resistance).

Thus if magnesium anodes are used the protection current density might exceed the protection current demand of the protected construction. Standards recommend application of magnesium anodes only for temporary protection of marine constructions [13]. Another factor limiting the usage of magnesium anodes is their low efficiency in seawater which is equal to high consumption rate [14].

Magnesium anodes are commonly used to protect underground structures and reinforced concrete [15–17] where on the contrary zinc and aluminium anodes are not used. Their potential versus steel is too low and due to this fact the protection current intensity is also low. The risk of overprotection if magnesium anodes are used is low because typical soil resistivity is high and greater than 100 Ωm. However, in a worst case scenario if soil has low electrical resistivity (i.e. waterlogged soils) and the coating is in a good condition (i.e. just installed gas tanks) the density of protection current might be too high and lead to an excessive polarization. Furthermore, an unreasonably high protection current supply can lead to an accelerated anode consumption and its shorter usability [18,19]. In such a case, it is advisable to lower the anode current outflow. In a typical galvanic anode cathodic protection system there is no means of protection current adjustment. Sometimes in order to reduce the protection current intensity resistors or diodes are used [20,21]. They are connected in a row between the protected structure and an galvanic anode.

In this paper a self-acting magnesium anode protection current regulation system, utilizing a bipolar transistor, is presented. If a transistor is properly connected it controls the protection current and does not allow for cathodic overprotection to take place. Another desirable effect is an extended magnesium anode life. The proposed technical solution can be applied both in earth and seawater, which extends the usability of magnesium anodes to seawater as well.

Zinc and aluminium anodes are usually cheaper than magnesium anodes however due to their high potential their application is limited to low resistivity environments. Thus magnesium anodes are more suitable for grounds and varying resistivity environments. The purpose of the transistor controlled CP system is to provide a passive driving system with overprotection protection for CP systems consisting of magnesium anodes.

In case of relatively small constructions susceptible to overprotection a transistor driven system would be more economic in comparison to ICCP systems. Maintenance and installation costs of galvanic anode systems are much lower compared to ICCP systems. On the other hand ICCP allows better potential control and is more sufficient for protection of relatively large constructions, for example long buried pipelines. Galvanic anodes are usually used for long term protection of coated structures. If protection current demand is too high their consumption would be very high and required anode mass would be uneconomic – ICCP system would be preferred. A medium power transistor would usually fit to control a single anode. If a greater protection current is demanded a higher power transistor should be applied.

2. Materials and methods

A potential of cathodically protected steel structure should not be more negative than −1.0 V against an Ag|AgCl|Seawater reference electrode. This value is close to the potential of zinc vs. Ag|AgCl|Seawater. This phenomenon can be used to control the protection current outflow from a magnesium anode. If a PNP transistor is used the following set up is realized: auxiliary zinc electrode connected to a transistor's base, a protected structure connected to an emitter and a magnesium anode connected to a collector. The connection scheme is presented in Fig. 1.

The system works as follows:

1. If the potential of the protected structure is more positive than an auxiliary electrode potential then an emitter–base voltage is positive and the transistor conducts the current flowing from the emitter to the collector. Thus current flows from the magnesium anode through an electrolyte to the protected structure.
2. If the construction is cathodically polarized its potential comes closer to the auxiliary electrode potential and the emitter–base voltage becomes lower. Thus, the emitter–collector current intensity is lowered and the cathodic protection current is lower.
3. The greater the potential difference is between the auxiliary electrode and the structure (the emitter–base voltage) the greater the current intensity from the galvanic anode is (the emitter–collector current intensity) and vice versa.
4. Once the protected structure reaches a desired potential (a limiting value of emitter–base voltage) the transistor stops to conduct current and the anode is disconnected. As a result the system will tend to uphold the structure potential close to the auxiliary electrode potential value.
5. If stray currents interfere [22] with the system and, depending on their polarization effect, either anodic or cathodic [23], the emitter–base voltage changes. Thus current intensity in the cathodic protection circuit changes too.

The application of auxiliary electrodes other than zinc is possible. Thus, polarization to the desired potential is possible. It is necessary for the auxiliary electrode potential to be more negative than the steel potential due to the fact that a positive value of emitter–base voltage is necessary. From the practical standpoint, it is most favourable to use zinc/seawater auxiliary electrode. An electrode made of pure zinc (>99.99%) has stable potential in seawater and is commonly used in marine cathodic protection systems.

All experiments were performed in a 3%NaCl water solution simulating a seawater environment. Prior and after the experiments, the water conductivity was measured in a four electrode arrangement using a soilbox and four electrode Nilsson soil resistance meter – Model 400.

Cubes made of magnesium alloy were cut. Their volume equalled 1 in.^{3} and the surface area equalled 6 in.^{2}. An electric connector was made of steel and the connection was sealed with silicon in order to eliminate galvanic couple between the connector and the specimen. Anodes were weighed before and after every experiment. Cathode was made of constructional S235JR steel mesh, which surface area equalled 0.075 m^2.

In electrochemical testing, an AD162 PNP transistor was used. Characteristics of the transistor were determined. The collector–emitter current was measured in a function of the base–emitter voltage at constant collector–emitter voltage. The base–emitter shunt equalled 165 kΩ and the collector–emitter shunt equalled 1 kΩ.

Magnesium anodes were tested in an arrangement proposed by the NACE Standard TM0190: "Impressed Current Laboratory Testing of Aluminium Alloy Anodes". Anodes were placed along the axis of cylindrical ϕ120 mm steel mesh. The system was immersed in a 3%NaCl water solution. Two electrode arrangements were proposed. In arrangement No. 1, no transistor or auxiliary driving electrode was used: the anode was directly connected to the steel mesh – the cathode. The potential of the steel mesh was measured against a Zn|ZnSO$_{4(sat.)}$ reference electrode. A 0.51 Ω shunt resistor was used to measure the protection current. In arrangement No. 2, a driving AD162 PNP transistor was used. Two experiments were conducted: using either a Zn|ZnSO$_{4(sat.)}$ or Zn|3%NaCl auxiliary electrode. The elements were connected as follows: steel mesh–emitter, magnesium anode–collector, either Zn|ZnSO$_{4(sat.)}$ or
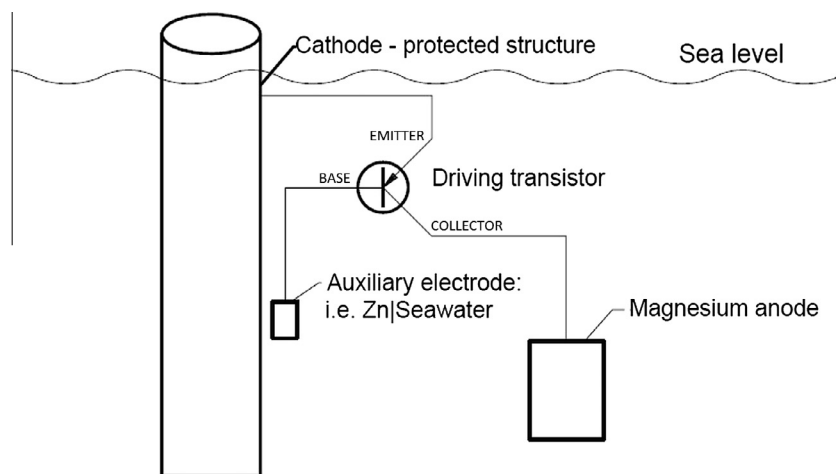
Fig. 1. Scheme of circuit connection.

Zn|3%NaCl electrode-base. The cell arrangement is presented in Fig. 1. A zinc electrode was mounted along a cylindrical steel mesh cathode. The protection current was measured across the 0.51 Ω shunt resistor. The potential of the steel mesh was measured against the electrode connected to the base of the transistor.

In order to investigate the performance of the transistor driven circuit with stray current interference laboratory tests were performed. The electrode arrangement as in Fig. 1 was chosen with Zn|ZnSO$_{4(sat.)}$ electrode connected to the base of the AD162 PNP transistor. The system was perturbed by an auxiliary potentiostat. Voltage was applied between two stainless steel electrodes introduced to the cell. The voltage was randomly changed in time and recorded. The potential of the protected steel sample and protection current were measured as well as the perturbation signal.

3. Results and discussion

Transistor characteristics are presented in Fig. 2. The lower the collector–emitter voltage is (cathode to anode potential difference – due to cathodic polarization of the protected structure) the lower the plateau current is. In that manner the transistor drives the anode current allowing only a limited amount of protection current to flow.
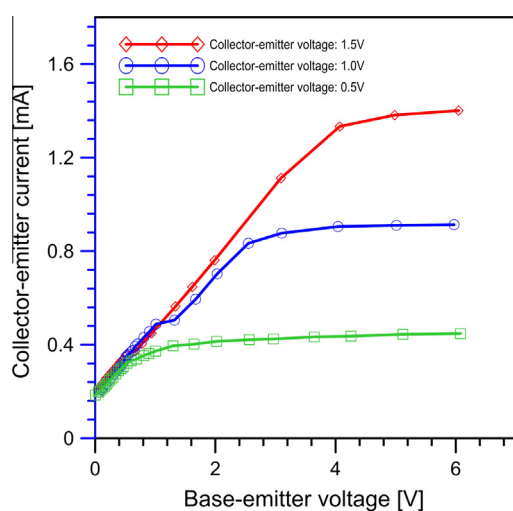
Typical potential and current time functions plots for non-driven and transistor driven cell setups are presented in Figs. 3 and 5. In Fig. 3, a plot for the direct magnesium anode to steel mesh (cathode) connection is presented. For the whole exposition duration potential of the protected mesh is proportional to the polarization current. The linear relationship between current and potential, in the investigated potential range, is presented in Fig. 4. The cathode potential ranges from −0.1 V to −0.2 V against Zn|ZnSO$_{4(sat.)}$, which means an excessive cathodic polarization (overprotection). The protection current intensity is very high and it ranges from 3.58 A/m^2 to 2.79 A/m^2. Due to high water conductivity, one could consider the protection circuit to be shorted. The potential of the cathode and the protection current at the beginning of the experiment are unstable and settle during the exposition as the anode is consistently consumed. It can be linked with an initial shorted circuit effect and stabilisation of working conditions over the exposition time. Very rapid electrochemical water decomposition to hydrogen occurred on the cathode surface throughout the experiment duration. After 72 hours' exposition, the anode was severely consumed (Fig. 7). The anode efficiency equalled approximately 65%. However, the real protection current demand is much lower in comparison to the current consumed by the system. The excessive current is wasted for water decomposition.
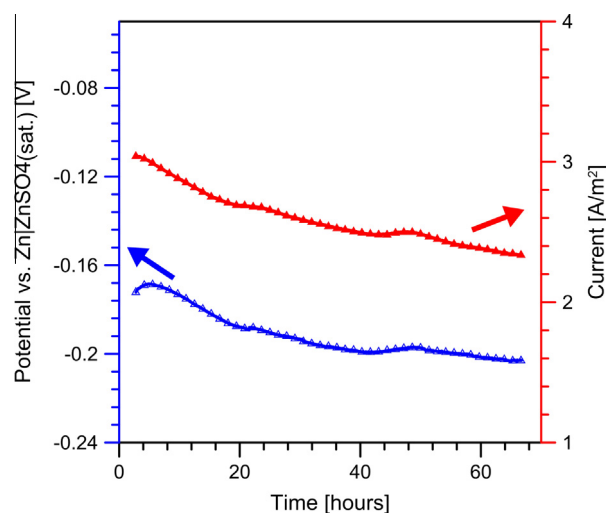

Fig. 2. Characteristics of AD162 PNP transistor used in the experiment.

Fig. 3. Cathode potential vs. Zn|ZnSO$_{4(sat.)}$ and protection current curves for direct anode to cathode connection electrochemical cell.
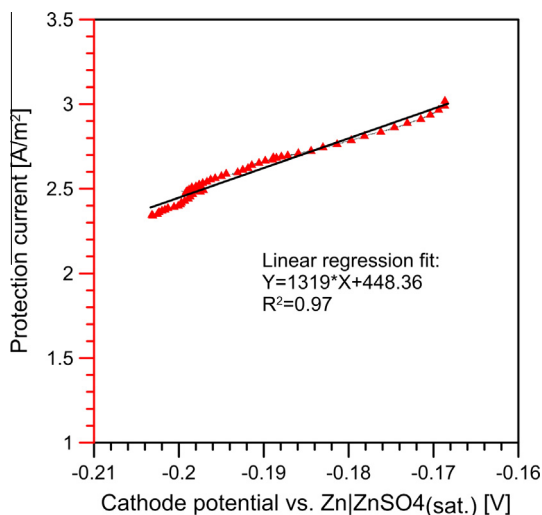
Fig. 4. The current–potential relationship. Coefficient of determination R^2 equalled 0.97.
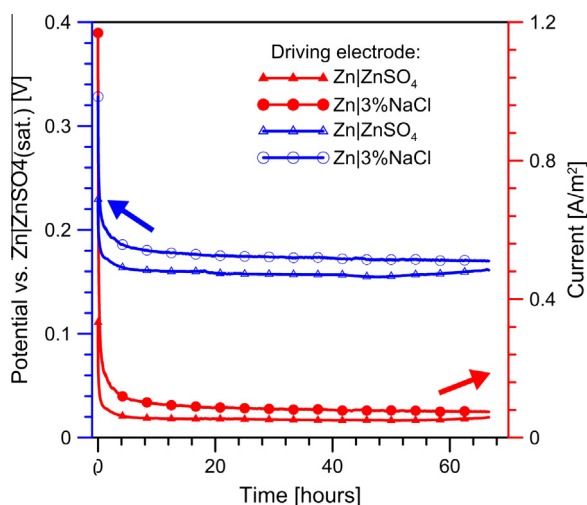

Fig. 5. Cathode potential vs. driving electrode (emitter–base voltage) and protection current curves for a transistor driven circuit.

Fig. 6. Samples – anodes after the exposition. Transistor driven (left) and without the transistor driving system (right).

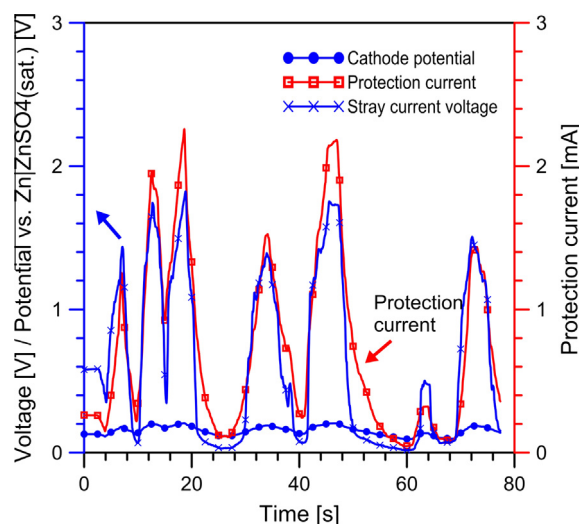**Fig. 7.** Protection current, cathode potential and voltage between the auxiliary stray current generating electrodes.

Thus, much of the anode's mass is wasted and results in uneconomical anode exploitation. Parameters of the anodes prior and after the exposition are presented in Table 1.

In Fig. 6, a typical potential and protection current curves in time for transistor driven circuit are presented. In comparison to direct anode connection, the initial potential of the cathode is higher. Over 3 h, the difference reaches 0.2 V. The final potential value which equals +0.17 V against a Zn|3%NaCl electrode connected to the base of the transistor or +0.16 against Zn|ZnSO$_{4(sat.)}$ electrode in the second experiment. The protection current was proportionate to the cathode potential and decayed from initial value as high as 1.06 A/m^2 or 0.20–0.074 A/m^2 or 0.060 A/m^2 for

Zn|3%NaCl and Zn|ZnSO$_{4(sat.)}$ base connected electrodes, respectively. Once the final potential was reached it was kept very stable during the exposition. The standard deviation of potential equalled 0.0019 V and 0.0015 V for Zn|3%NaCl and Zn|ZnSO$_{4(sat.),}$ respectively base connected electrodes. The final cathode potential against Ag|AgCl|3%NaCl equalled approximately either −0.83 V or −0.84 V for respective driving electrodes. According to DNV RP-B401-2011: "Cathodic protection design", a potential below −0.8 V against Ag|AgCl|3%NaCl reference electrode is accepted as design protective potential for carbon and low-alloy steels. The electric charge transferred between the anode and the cathode in the transistor driven cell was from 30 to 60 times lower as compared to the non-driven cell (Table 1).

A visual inspection of the cathodes and anodes clearly proved that the transistor successfully increased the anode longevity and efficiency (Fig. 6). Without the transistor, the magnesium anode was severely consumed and the electrochemical cell was filled with magnesium corrosion products. For short exposition times, the real anode current output for transistor driven circuit mass

Table 1

Experiment data for tested electrochemical cell arrangements.

	Direct anode–cathode connection Zn|ZnSO$_{4(sat.)}$	Transistor driven Zn|ZnSO$_{4(sat.)}$	Transistor driven Zn|3%NaCl
Estimated operating time of 1 kg anode	9.5 months	60 years	30 years
Theoretical anode current output (A h/kg)	2205.88		
Real anode current output (A h/kg)	1433.55	1733.74	1777.05
Consumption rate (kg/A year)	6.11	5.05	4.92

calculations was burdened with a great error due to a very low mass loss of the anode. However, the point that the anode service time is greatly enhanced while providing a proper degree of protection is proven and the calculated efficiency equalled approximately 79%. The anode current output is defined as a charge which an anode can supply per its 1 kg weigh. In practise it is expressed in Amperes times hour per kilogram-Ah/kg. The real anode current output for direct anode–cathode connection is in agreement with the literature – 1420 Ah/kg, which corresponds to 65% efficiency [24].

I_{RAC} – Real anode current output (Ah/kg) was calculated from the following relationship (Eq. (2)):

$$I_{RAC} = \frac{C}{\Delta m} (A * h/kg) \tag{2}$$

where C is the total electric charge transferred (Q), Δm is weight loss (kg).

The C_r – consumption rate was calculated from the following relationship (Eq. (3)):

$$C_r = \frac{8760}{\text{Real current } output} (kg/A * year) \tag{3}$$

In order to present the application of the transistor in a more appealing way, an estimated operating time of 1 kg of magnesium anode, based on the weight loss, was calculated. Without a transistor driven circuit, 1 kg of magnesium sacrificial anode would last for 9.5 months. For a transistor driven circuit, depending on the driving electrode used, the anode would last for 30 or 60 years.

The results of the stray current interference simulation with an external current source are presented in Fig. 7. If an external signal interferes with the cathode the driving electrode-cathode voltage changes. Changes in both the cathode potential and the protection current are correlated to the external perturbation signal. If the stray current interference is anodic, the protection current is increased due to an increase in the emitter–base voltage. If the stray current interference is cathodic the protection current demand is lower and the transistor is shut due to the lowered emitter–base voltage. Thus, this is a self-regulating system. Without the transistor control system a magnesium anode would provide an excessive protection current until potential of the construction is polarized to the anode potential.

4. Conclusions

The application of a transistor with a properly chosen auxiliary driving electrode proved to reduce the current output from a magnesium anode in seawater or waterlogged soil environments. The proposed electrode arrangement is a self-regulating system. A visual and mass examination proved that the efficiency and operating time of the magnesium anode was enhanced in comparison to a transistor non-driven circuit. Overprotection causing hydrogen embrittlement and a loss of anode electrochemical energy was eliminated. The potential of the cathode was kept below the generally accepted level of −0.8 V against the Ag|AgCl|3%NaCl reference electrode. For both of the tested auxiliary driving electrodes (Zn|3%NaCl and Zn|ZnSO$_{4(sat.)}$), the cathodic protection criterion was met. Their selection was crucial to drive the potential of the cathode. The expected anode operating time was calculated. For a transistor driven system, depending on the driving electrode used, it was estimated to be 37–75 times longer in comparison to a direct anode to cathode connection. Laboratory testing also indicates that the proposed method is useful if there is possible stray current interference. Magnesium anodes, due to their lightweight and high current output, are an attractive material. The application of a transistor could help to utilize them in a seawater environment.

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