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Electrochemical properties of composite anodes for cathodic protection

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Abstract

Comparative results of electrochemical investigations of polymeric composites with different contents of carbon black and graphite activated with ruthenium oxides are presented. Electrochemical impedance measurements (EIS), enabling determination of electrical and electrochemical properties of polymeric composites, were accompanied by potential measurements performed during a 21-day galvanostatic polarization at 5 A m^{-2} current density. Gravimetric measurements were also made to determine the extent of anode consumption. It was demonstrated that the presence of ruthenium oxides characterised by high electrocatalytic activity in the polymeric composites causes an improvement in the polarisation characteristics, a decrease in the value and improvement in stability of the potential during long-term operation, and also a decrease in the anode consumption, as compared to composites exclusively containing activated carbon black.

1. Introduction

In the mid-1980s, elastic anode cables appeared in active cathodic protection systems. This solution permitted positioning the anodes in close proximity to the protected structure, thus minimizing the interference hazard to neighbouring buried objects [1]. Additionally, these anodes guaranteed a uniform current density distribution, and made possible the protection of several pipelines with the use of a single anode. This is of great significance with increasing underground urbanisation. The wider application of cable anodes, that is, in the protection of reinforced concrete structures [2], buried pipelines etc., reflects the considerable practical importance of this approach. Attempts have been made to use conducting polymers in cathodic protection of marine piling. The results indicate that these materials are effective as anodes for suppressing corrosion in the tidal areas [3]. The range of applications of conducting polymers in cathodic protection will undoubtedly increase.

Construction of a cable anode is relatively simple; it is made of a copper wire surrounded by electrically conducting polymeric material, the latter constituting an essential part of the anode [4, 5]. The polymeric composite contains different carbon based materials (conducting fillers). Depending on the applied conducting fillers, mixtures of various electrical and electrochemical properties can be obtained. Due to continuous anodic oxidation of carbon under operating conditions, it is necessary to use larger initial amounts of fillers in the polymeric mixtures to extend the lifetime of the anodes.

Severe anode working conditions in cathodic protection systems force such a choice of polymeric composite that guarantees many years of trouble-free operation of cable anodes. Electrochemical and exploitation investigations of composite electrodes have pointed to the need for new composites containing modified conducting components, facilitating the process of oxygen or chlorine evolution and limiting the oxidation process of carbon [6, 7]. Thus, this work is a continuation of earlier studies on improving the electric and electrochemical parameters of polymeric composites through introduction of fillers activated by an addition of electrochemically active ruthenium oxides [8, 9].

The aim of this work is the comparison of electrochemical properties of composite polymeric electrodes with and without the modified component.

2. Experimental details

Composite electrodes based on the ethylene–propylene terpolymer (EPDM–ethylene–propylene–diene–monomer) matrix, characterized by good resistance against the action of oxidizing conditions and many chemical media, were investigated in this study.

The following conducting components were used: P-1250 acetylene carbon black (referred to as AB); highly conductive Chezacarb EC carbon black (EC); electrographite (GR); and electrographite modified with $Ru_{0.3}Ti_{0.7}O_2$ (RU/GR).

The graphite was subjected to preliminary drying and, subsequently, two mesh fractions were obtained: <0.064 mm and from 0.064 to 0.071 mm. Both fractions were used for modification at a 1:1 (w/w) ratio. The graphite was treated with a solution containing ruthenium chloride ($RuCl_3$) and titanium chloride ($TiCl_3$) at a 3:7 molar ratio. The obtained slurry was dried at 150 °C for 1.5 h. The dried powder was then kept in an oven at 420 °C for 15 min, during which ruthenium chloride and titanium chloride converted to the corresponding oxides. The operation was repeated (lasting one hour), to assure complete chloride-to-oxide conversion.

The following additional components were used in the polymer mixtures: vulcanizing substances, plasticizers, antiageing substances and a vulcanizing accelerator [10]. The mixing process was carried out in a rolling mill, and vulcanization in a press at 160 °C for 20 min. Sheets of conducting composite (~3 thickness) were obtained [6, 7]. Discs for investigation were cut out and placed in plexiglas holders providing a working area (geometric) of 5 cm^2.

The compositions of the obtained composites are listed in Table 1. The contents of added components are given per 100 parts of polymer (w/w).

The electrochemical investigations consisted in long-term galvanostatic anodic polarization of each composite sample in 0.1 M Na_2SO_4 solution at ambient temperature. During exposure the potential of samples was recorded every 24 h against a saturated calomel electrode (SCE) placed in a Lugin capillary. A platinized titanium mesh was used as the auxiliary electrode.

A model Atlas 9232 (Atlas–Sollich, Poland) computer controlled multichannel galvanostat–potentiostat was used for the measurements.

Investigations were performed at a current density of 5 A m^{-2} for 21 days. The cell was switched over periodically to the model Atlas 88 computer controlled electrochemical set-up and electrochemical impedance spectra of polarized samples were determined. The same current densities were used as in the galvanostatic investigations. After completing the exposure, measurements of the mass of the samples were carried out to determine their weight losses.

3. Results and discussion

The changes of potential of a number of composite anodes during the long-term (21 days) galvanostatic polarization at a 5 A m^{-2} current density are shown in Figure 1(a). Potentials of samples with the lowest carbon black contents (50EC-0AB-0GR-0RU/GR and 30EC-50AB-0GR-0RU/GR) increase significantly during exposure and, after several or a dozen days, attain values (above 15 V) eliminating the samples from further investigation. The remaining samples, containing more carbon black, were characterized by a lower potential, having a tendency to a slight increase with time.

In Figure 1(b), potential changes of electrodes containing modified graphite (RU/GR) during exposure are presented. The result for a sample of composition 50EC-0AB-50GR-0RU/GR (the sole sample containing no modified graphite the potential behaviour of which, under galvanostatic polarization conditions, does not exclude it from further investigations) has been shown for comparison. The other electrodes display the desired feature of anodes operated in cathodic protection systems, that is, a constant (moderately stable) potential. The results suggest that even a small quantity of ruthenium oxide modified graphite decreases the measured potential by as much as 400–500 mV. This effect is amplified when a larger quantity is applied. Application of modified material positively affects the potential–time stability, and even results in a gradual decrease of potential after certain period of polymer operation under current conditions. Therefore, its application positively affects the stability of the polymeric material and may be noticed when comparing potential-time curves for samples without the modifier with those for samples containing the modified component. The decrease in potential is connected with a decrease in the *IR* ohmic drop. Smaller resistivity also leads to a decrease in the current required for the proper protection of a structure in the case of a cable anode containing the modified component.

Impedance measurements were carried out in order to evaluate the effect of active oxides on the impedance of the composite material, as well as on the impedance of the oxygen evolution reaction. The impedance spectrum

Table 1. Characteristics of composites used in the study

Symbol of composite	Basic composition, parts by weight per 100 parts of the polymer base material			
	Highly conductive black	Acetylene black	Electrographite	$Ru_{0.3}Ti_{0.7}O_2$ modified electrographite
50EC-0AB-50GR-0RU/GR	0	0	50	0
50EC-0AB-0GR-0RU/GR	50	0	0	0
30EC-50AB-0GR-0RU/GR	30	50	0	0
30EC-100AB-0GR-0RU/GR	30	100	0	0
30EC-150AB-0GR-0RU/GR	30	150	0	0
50EC-0AB-0GR-50RU/GR	50	0	0	50
50EC-0AB-0GR-100RU/GR	50	0	0	100
50EC-0AB-0GR-150RU/GR	50	0	0	150

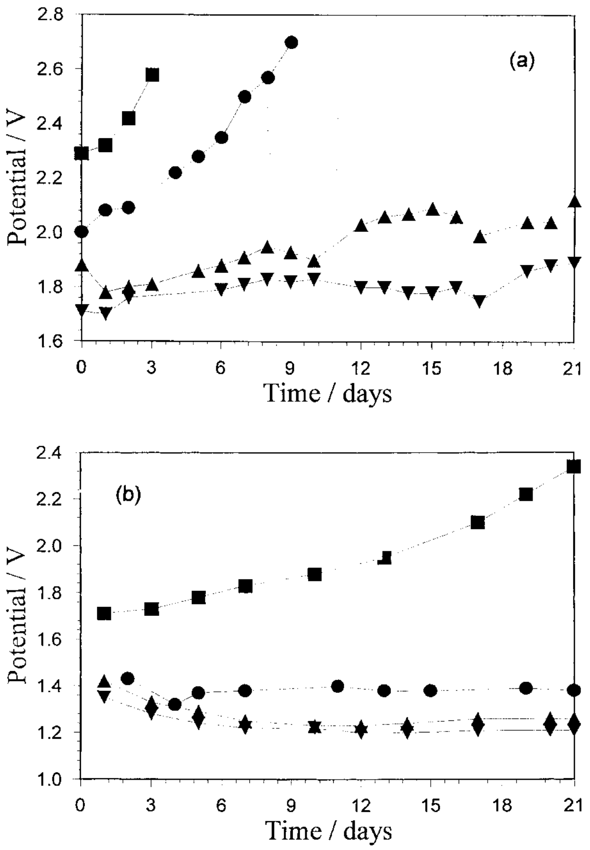

Fig. 1. Potential changes of polymeric conductive composites during galvanostatic anodic polarization at 5 A m^{-2} current density. *Key*: (a): (■) 50EC-0AB-0GR-0RU/GR; (●) 30EC-5AB-0GR-0RU/GR; (▲) 30EC-100AB-0GR-0RU/GR; (▼) 30EC-150AB-0GR-0RU/GR. (b): (■) 50EC-0AB-50GR-0RU/GR; (●) 50EC-0AB-0GR-50RU/GR; (▲) 50EC-0AB-0GR-100RU/GR; (▼) 50EC-0AB-0GR-150RU/GR.

of the composite electrode is rather complex. It is associated with the heterogenic structure of the electrode, particularly with chemical and physical heterogeneity of its surface. Thus, in the impedance spectrum, several time constants can be distinguished, characterised by different dependencies on potential [11]. The high-frequency part of the impedance spectrum takes the shape of a flattened semicircle, independent of the polarizing current density. As shown in earlier investigations, its size depends primarily on the conductivity of the composite [6]. The resistance (R_c) of the first semicircle, determined by computer analysis, describes the bulk resistance of the composite electrode and characterises its electrical properties. This parameter is very useful for the evaluation of electrical properties of the composite electrodes and for the assessment of their performance parameters during anodic polarization. The low-frequency part of the impedance spectrum depends on the current density and describes the course of the electrochemical reactions.

Examples of the impedance spectra for composite electrodes during long-term anodic polarization are given in Figure 2(a)–(d), while the values of the resistance of the composite electrodes, calculated by computer analysis of the spectra, are summarized in Table 2

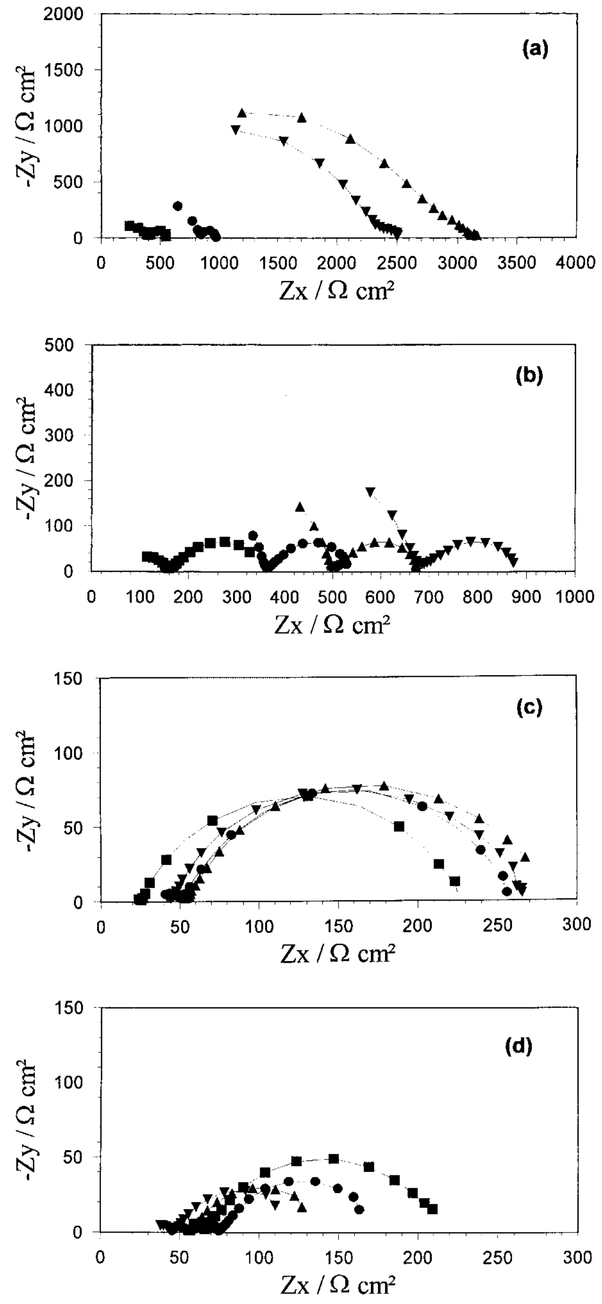

Fig. 2. Electrochemical impedance spectra of polymer composites determined under conditions of galvanostatic anodic polarization at 5 A m^{-2} current density. *Key*: (a): 30EC-50AB-0GR-0RU/GR; (b) 30EC-100AB-0GR-0RU/GR; (c) 50EC-0AB-0GR-50RU/GR; (d) 50EC-0AB-0GR-150RU/GR. *Duration*: (■) 1, (●) 7, (▲) 14 and (▼) 21 days, except for (a) when ▼ represents 13 days.

[12]. In the case of electrodes containing the nonmodified carbon material, the high-frequency fragment of the spectrum (R_c) increases with time and shifts towards higher Z_x values. This is associated with the carbon oxidation process, occurring in accordance with the total reactions:

$$C + 2\,H_2O \rightarrow CO + 2\,H^+ + 2\,e^- \quad (1)$$

$$C + 2\,H_2O \rightarrow CO_2 + 4\,H^+ + 4\,e^- \quad (2)$$

Table 2. Changes in resistance of composite as a function of time during long-term anodic polarization in 0.1 M Na_2SO_4; $i = 5$ A m^{-2}

Sample	Measurement time/days (R_c/Ω cm^2)			
	1	7	14	21
50EC-0AB-50GR-0RU/GR	240	450	680	990
50EC-0AB-0GR-0RU/GR	400	1550	–	–
30EC-50AB-0GR-0RU/GR	400	2350	3100	–
30EC-100AB-0GR-0RU/GR	160	360	500	680
30EC-150AB-0GR-0RU/GR	40	220	240	280
50EC-0AB-0GR-50RU/GR	205	210	220	225
50EC-0AB-0GR-100RU/GR	165	105	95	90
50EC-0AB-0GR-150RU/GR	155	85	80	75

Although in a 0.1 M Na_2SO_4 solution the oxygen evolution reaction is the dominating process, during long-term anodic polarization the effect of the carbon oxidation process becomes apparent [11]. In the case of samples containing relatively low quantities of carbon material (50EC-0AB-0GR-0RU/GR and 30EC-50AB-0GR-0RU/GR, Figure 2(a) and Table 2), the resistance of the composite increases rapidly. A loss of the conducting carbon material at the surface, leading to an increase in the resistivity of the composite, is the probable cause of this phenomenon. In the case of samples containing larger quantities of carbon material, the increase in resistivity is not so high (Figure 2(b)). The spectra of composite electrodes containing modified graphite are characterized by a very small increase in resistance (Figure 2(c)), and at larger quantities of modified graphite, even by a decrease in resistance R_c as a function of polarization time (Figure 2(d) and Table 2). The results emphasise the beneficial effect of modified carbon material on electrical parameters of investigated composites.

The gravimetric measurements provide an additional test characterizing the operational properties of the anode materials. Results, compiled in Table 3, indicate a significant influence of modified filler on the increase in stability of polymeric composites. The weight loss of nonactivated samples is comparable to that of traditional graphite anodes used in cathodic protection systems. The presence of ruthenium oxide modified graphite reduces the losses of polymeric material caused by a flow of a unit of electric charge (A year, Table 3) by approximately one order of magnitude, and therefore prolongs the anode lifetime. Hence, the introduction of active oxides into the composite, although increasing the cost of polymeric anode, results in improvement of its operating parameters.

Table 3. Weight loss of composite electrodes after long-term anodic polarization

Sample	Weight loss/(g A^{-1} $year^{-1}$)*
50EC-0AB-50GR-0RU/GR	430
50EC-0AB-0GR-0RU/GR	–
30EC-50AB-0GR-0RU/GR	–
30EC-100AB-0GR-0RU/GR	412
30EC-150AB-0GR-0RU/GR	296
50EC-0AB-0GR-50RU/GR	16
50EC-0AB-0GR-100RU/GR	10
50EC-0AB-0GR-150RU/GR	22

*Weight loss was determined by mass measurements of electrodes at the constant current load per unit of time

The gravimetric measurements also indicate that, when designing polymeric composites for construction of cable anodes based exclusively on the conducting carbon filler, it should be introduced in larger quantities to compensate for losses resulting from carbon oxidation.

4. Conclusions

Anodic properties of conducting polymeric composites, based on the ethylene–propylene (EPDM) terpolymer and designed for cathodic protection systems, depend, amongst other factors, on the contents of admixed carbon material. This quantity has an effect on the resistivity of the composite while, simultaneously, the carbon based filler undergoes gradual oxidation under long-term polarisation. At low initial contents of carbon material, a significant increase in the resistance of the anode occurs with time. Therefore, the use of a higher initial contents of conducting carbon material is recommended. On the other hand, an excessive quantity of the filler has a disadvantageous effect on the mechanical properties of the composite [10]. The presence of oxides characterized by high electrocatalytic activity in the polymeric composite results in an improvement in polarization characteristics, a decrease in potential and improvement in its stability during long-term operation, and also in a decrease in anode consumption due to the anodic oxidation of carbon. The addition of modified carbon material also enables optimum electrochemical and electrical parameters at significantly lower filler contents. Until recently, in cathodic protection practice it was recommended to avoid working current densities higher than 0.5 A m^{-2} for composite anodes and cases of anode damage were explained as due to the excessive local current density [13]. During formulation of recipes for composite electrodes to be used as anodes in cathodic protection systems, it seems justified to apply a modified carbon material, the presence of which could result in an increase in the current-carrying capacity of cable electrodes.

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