Performance improvement of direct methanol fuel cells *via* anodic treatment using various organic acids

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Abstract−Performance improvement of direct methanol fuel cells (DMFCs) was achieved *via* an anodic treatment technique. Previously, anodic treatment was performed using sulfuric acid as acidic media, but various organic acids including formic, acetic, oxalic, and citric acids were employed in this study to avoid the use of toxic sulfuric acid. By replacing sulfuric acid to organic acids, a potential damage to catalyst layers and other components such as polymer electrolyte membrane and bipolar plates are expected to be minimized. The anodic treatment was performed by applying 0.7 V (vs. reversible hydrogen electrode) at the anode of DMFCs flowing the organic acid solutions for 30 min. After the anodic treatment, peak power densities of DMFCs were increased by +7, +32, +23, and −2.6% when formic, acetic, oxalic, and citric acid solutions were employed, respectively. The enhanced catalytic activity of the DMFCs in the acetic and oxalic acid solutions was confirmed by analyzing electrochemical impedance spectroscopy data.

Key words: Direct Methanol Fuel Cell, Methanol Electro-oxidation, Electrocatalyst, Electrochemical Impedance Spectroscopy, PtRu

INTRODUCTION

Methanol electro-oxidation reaction (MOR) is a hot research issue owing to its importance in direct methanol fuel cell (DMFC) application. DMFC is an electrochemical device which converts chemical energy of methanol and oxygen into electricity. The use of methanol in DMFC enables volume reduction and easy transportation, while other fuel cells which employ hydrogen instead of methanol suffer from handling and transportation of hydrogen gas. But the use of methanol has also some drawbacks, such as low activity of the MOR catalysts and cross-over of methanol from the anode to the cathode electrode [1].

Currently, binary Pt-Ru alloy is widely used for the MOR, because it could significantly improve poor activity of Pt catalyst which was first introduced for the MOR [2-4]. Despite the improved MOR activity of the PtRu catalyst, commercial requirements are not satisfied yet because of high cost and low activity. Major efforts have been devoted to development of PtRu based ternary or quaternary catalysts such as PtRuFe [5-7], PtRuW [8-13], PtRuCo [7,10], PtRuNi [14-16] and PtRuMoW [17]. These catalysts could significantly improve the MOR activity of PtRu by the addition of transition metals, but stability, especially for the transition metals, and mass production of homogeneous composition might need more research for commercialization of these catalysts.

Besides from these efforts, it was also reported that the activity of the PtRu catalyst could be significantly improved by an electro-

chemical process, the so-called anodic treatment [18]. The anodic treatment method was introduced by Lu et al. [18], where the MOR activities of various PtRu catalysts increased by five times by anodic treatment, which was performed by applying a potential of 1.3 V (vs. reversible hydrogen electrode (RHE)) for 30 min. The authors have suggested that the formation of reversible Ru (hydrous) oxides, which are beneficial for the MOR, and a decrease of irreversible Ru (hydrous) oxides which are harmful for the MOR resulted in the improved MOR activity. Jeon et al. [19] applied the anodic treatment to a single cell and could achieve 48% increase in peak power density of the single cell. In the previous study [19], the authors suggested that formation of hydrous Ru oxide by the anodic treatment led to the enhanced MOR activity of the PtRu catalyst. In addition, other reports also showed that Ru hydrous oxide is more active for the MOR than metallic Ru, while the contribution of RuO_2 was far less than both [19-26]. These results suggest that anodic treatment is a useful method to maximize the performance of commercial PtRu catalysts by tuning the surface properties of Ru in a simple manner.

Although it was shown that anodic treatment can improve the performance of DMFCs, the use of sulfuric acid with an applied potential can cause damages to other cell components such as support material, bipolar plate, and polymer electrolyte membrane. In the present study, we investigated organic acids including acetic, oxalic, and citric acids to replace highly toxic sulfuric acid to lessen the potential damages caused by the anodic treatment. These organic acid solutions have higher pH values of 2.4, 1.8, and 3.6 for 1 M of acetic, oxalic, and citric acids, respectively, meaning that the potential corrosion of carbon support or bipolar plates can be lessened when compared to sulfuric acid case (pH is 0.0 for 1 M solution). Formic acid was especially employed in addition to the above acids to verify if it can work as both fuel and anodic treatment medium because it is a well known fuel of direct formic acid fuel cells. A

quantitative analysis of DMFC single cells was performed by employing electrochemical impedance spectroscopy (EIS) technique before and after the anodic treatment experiments.

EXPERIMENTAL

1. Fabrication of Membrane-electrode-assemblies (MEAs)

Commercial PtRu black (HiSPEC6000, Johnson Matthey, U.K.) and Pt black (HiSPEC1000, Johnson Matthey, U.K.) catalysts were employed as the anode and cathode catalysts, respectively. Catalyst inks were prepared by mixing catalyst, de-ionized (DI) water, isopropyl alcohol, and Nafion ionomer solution. The inks were put through sonication to achieve homogeneous mixing. The prepared catalyst inks were sprayed onto poly(tetrafluoroethylene) (PTFE) sheets until catalyst loading of 2 mg/cm^2 was obtained. The MEAs were fabricated by hot-pressing the Nafion115™ membrane (DuPont) sandwiched by the PTFE sheets coated with the anode and cathode catalyst inks. The hot-pressing was performed at 120 °C for 3 min. and then the PTFE sheets were removed leaving the catalyst layers on both sides of the Nafion membrane. Active area of the MEAs was 4 cm^2.

Operation of the MEAs was performed by feeding 1 M methanol solution at a flow rate of 1 mL/min and oxygen at a flow rate of 100 cc/min to the anode and cathode electrodes, respectively. The cells were kept at 55 °C through the whole operation.

2. Anodic Treatment and Measurement of EIS

Anodic treatment was performed by keeping the potential of the anode electrodes at 0.7 V for 30 min. During the anodic treatment, 1 M acid solution (1 mL/min) and dry hydrogen (30 cc/min) were fed into the anode and cathode electrodes, respectively. The cathode electrode functioned as both the counter and reference electrode.

EIS was measured by varying frequency from 10^5 to 0.01 Hz using a Solartron 1255B frequency response analyzer. During the measurements, a current density of 100 mA/cm^2 was applied to the MEAs, and methanol (1 M, 1 mL/min) and oxygen (100 cc/min) were fed into the anode and cathode electrodes, respectively.

3. Half Cell Reaction of the PtRu Catalyst

Half cell testing was performed by making a catalyst thin film on a glassy carbon electrode (3 mm diameter, BAS Co. Ltd., MF-2012). To make the catalyst thin film, catalyst ink was prepared by mixing the PtRu catalyst with de-ionized water and 5 wt% Nafion ionomer solution. The mixture was put through sonication to achieve homogeneous mixing. The resulting catalyst dispersion was dripped on the glassy carbon electrode. After drying in the air, 5 wt% Nafion ionomer solution was dripped on the catalyst layer to provide mechanical strength to the catalyst layer. Loading of the catalyst was 13.9
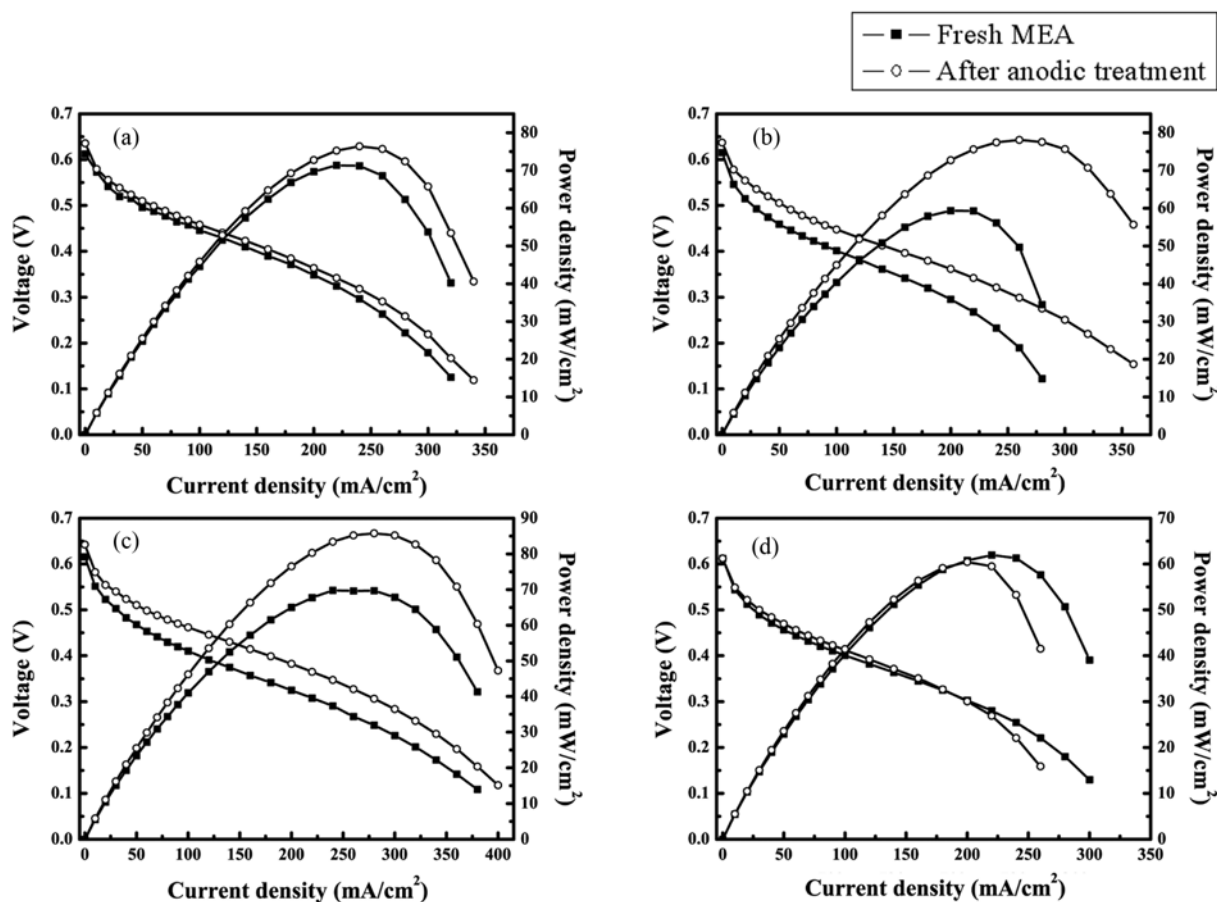

Fig. 1. The I-V testing results before and after the anodic treatment which was performed by applying a potential of 0.7 V at the anode electrode for 30 min. flowing various acidic solutions of (a) formic acid, (b) acetic acid, (c) oxalic acid, or (d) citric acid at a flow rate of 1 mL/min. A temperature of the single cells was kept at 55 °C, and dry hydrogen was fed into the cathode electrode at a flow rate of 30 cc/min.

mg/cm^2. Linear sweep voltammetry was performed by increasing the potential from 0.1 to 0.5 V (vs. reversible hydrogen electrode (RHE)) at a scan rate of 1 mV/s. 1 M H$_2$SO$_4$+1 M methanol solution was used as the electrolyte. Before the linear sweep voltammetry testing, the electrolyte solution was purged by N$_2$ gas for 1 h. Platinum wire and Ag/AgCl electrode (BAS Co. Ltd., MF-2052 RE-5B) were employed as the counter and reference electrodes, respectively. All potentials in this paper were converted into RHE scale.

RESULTS AND DISCUSSION

Fig. 1 shows the I-V measurement results of four single cells which were anodically treated using various organic acid solutions. The peak power density of each cell increased by +7, +32, +23, and −2.6% for the cells treated by using formic, acetic, oxalic, and citric acid, respectively. Note that an identical potential (0.7 V) and time (30 min) were applied for all cells. Although the peak power densities were not improved as much as the sulfuric acid case (+48% improvement) [19], these results clearly show that the anodic treatment is dependent on the acidic medium, and acetic and oxalic acids have the potential to replace toxic sulfuric acid. As a DMFC single cell is a complicated electrochemical device, it is not clear how the anodic treatment contributed to the improved performance. An EIS analysis technique was employed for a quantitative performance analysis of the single cells.
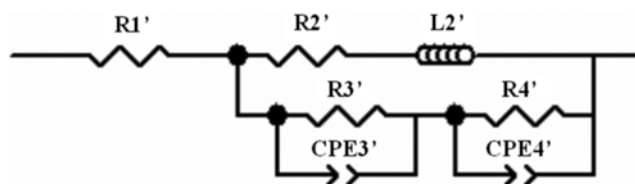

Fig. 2. The equivalent circuit employed for the simulation of EIS measurement results (reprinted from [27] with a permission of Elsevier).

An analysis of the EIS measurement results requires an equivalent circuit which describes the electrochemical system to be analyzed. In the present study, we employed an equivalent circuit which was previously suggested by Jeon et al. [27] for the analysis of DMFCs (shown in Fig. 2). In the equivalent circuit, R1' represents an IR resistance, while R2' is CO$_{ads}$ oxidation reaction resistance. R2' is related to both R3' and R4' which represents methanol electro-oxidation and oxygen electro-reduction reaction resistances, respectively, because oxidation of CO$_{ads}$ occurs both at the anode and cathode electrodes owing to methanol cross-over from the anode to cathode electrodes. L2' is an inductive element that represents phase delay caused by a slow relaxation of CO$_{ads}$ [28]. CPE3' and CPE4' are capacitive components that include diffusion effect. The CPE (constant phase element) consists of two values of CPE-T and CPE-P which represent capacitance (T) and nonhomogeneity (P) con-
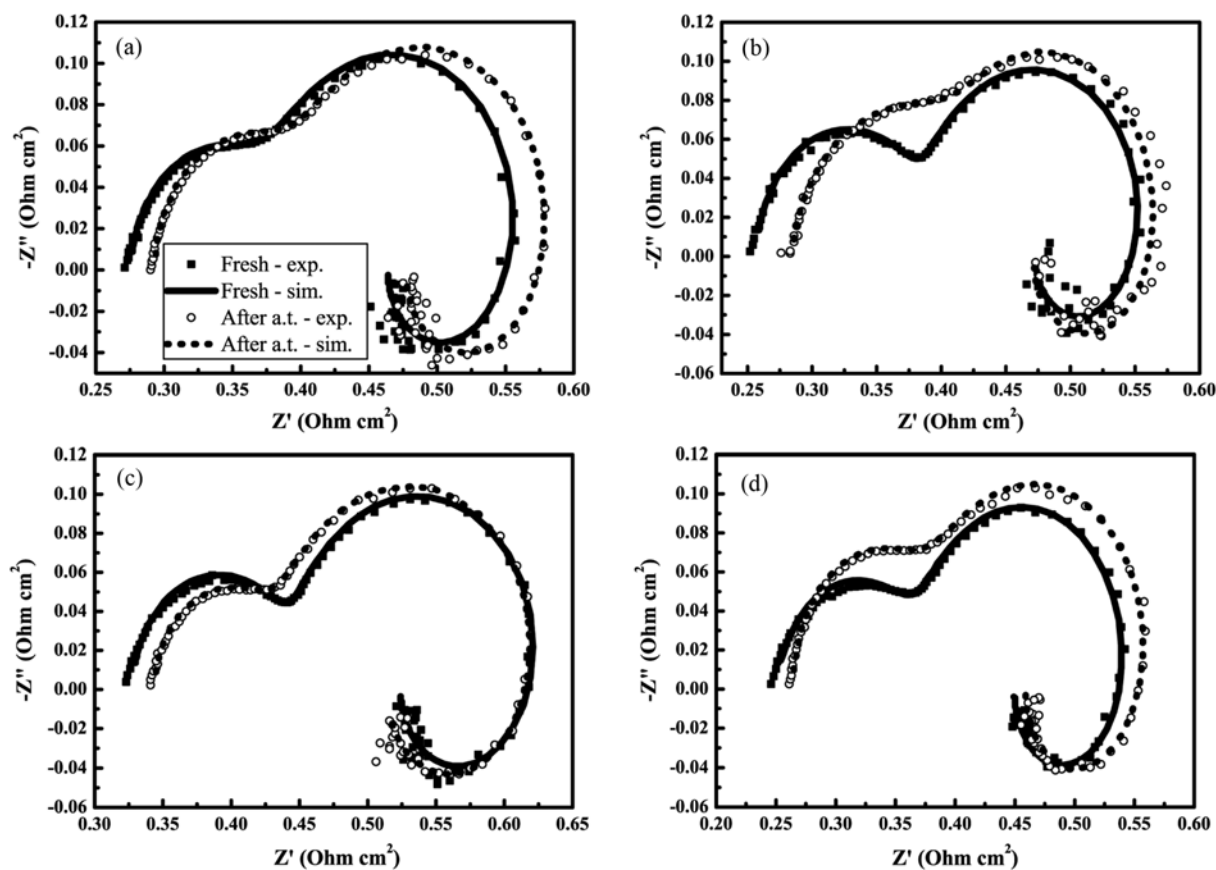

Fig. 3. The EIS measurement and simulation results for the cells anodically treated with a flow of (a) formic acid, (b) acetic acid, (c) oxalic acid, or (d) citric acid.

Table 1. Summary of the EIS data simulation results and the peak current densities

	Formic acid		Acetic acid		Oxalic acid		Citric acid	
	Before	After	Before	After	Before	After	Before	After
R1' (Ω cm^2)	0.275	0.293	0.256	0.284	0.327	0.344	0.250	0.264
R2' (Ω cm^2)	0.407	0.363	0.581	0.551	0.412	0.328	0.503	0.432
L2' (H/cm^2)	0.257	0.233	0.460	0.833	0.348	0.282	0.507	0.313
R3' (Ω cm^2)	0.249	0.275	0.215	0.134	0.262	0.264	0.210	0.241
CPE3'-T (F/cm^2)	0.794	0.819	0.874	0.744	1.07	0.996	0.830	0.736
CPE3'-P	0.978	0.957	1.00	1.17	0.969	0.965	0.971	0.971
R4' (Ω cm^2)	0.103	0.0993	0.130	0.149	0.116	0.0891	0.120	0.111
CPE4'-T (F/cm^2)	0.108	0.111	0.0452	0.164	0.0481	0.0978	0.0578	0.0825
CPE4'-P	0.940	0.981	0.946	0.903	0.952	0.966	0.886	1.00
Reaction resistance[a] (Ω cm^2)	0.188	0.185	0.216	0.187	0.197	0.170	0.199	0.194
Peak power density (mW/cm^2)	71.4	76.4	59.3	78.1	69.7	85.8	62.0	60.4

[a]Calculated by (R2×(R3+R4))/(R2+R3+R4)

stants, respectively. The CPE is expressed as

$$Z = \frac{1}{T\sqrt{\omega^P}} \qquad (1)$$

Fig. 3 shows the EIS measurement and simulation results performed using the equivalent circuit mentioned above. The simulation results are summarized in Table 1. In the table, it is interesting to compare the changes of the IR resistance (R1'). Previously, it was shown that the IR resistance increased by 7.03% when a sulfuric acid solution was employed for the anodic treatment [19]. All R1' values of the present study also increased by 6.55, 10.94, 5.20, and 5.60% for the formic, acetic, oxalic, and citric acid solutions, respectively. As noted in the introduction, the purpose of this study is to replace highly toxic sulfuric acid by milder organic acids to minimize the potential damage against other components. The increased IR resistance values suggest that a negative effect was caused by the anodic treatment on the IR resistance related components. The acetic acid case exhibited the highest IR resistance increase, although it is a mild acid with a relatively high pH of 2.4. It is not clear which part of the IR resistance component was affected by acetic acid; however, these results suggest that acetic acid is not promising as the anodic treatment medium owing to its negative effect on other components. On the other hand, oxalic acid exhibited the lowest increase in the IR resistance, suggesting that oxalic acid is a promising alternative to sulfuric acid. The reaction resistance that includes all reaction resistance components (CO$_{ads}$ oxidation (R2'), methanol electro-oxidation (R3'), and oxygen electro-reduction (R4')) was calculated from the simulation results by combining R2', R3', and R4' through the following equation:

$$\text{Reaction resistance} = (R2' \times (R3'+R4'))/(R2'+R3'+R4') \qquad (2)$$

The reaction resistance values showed a good agreement with the change of peak power densities. In the case of acetic acid treated cell, the reaction resistance decreased from 0.216 to 0.187 Ω cm^2, and, at the same time, peak power density increased from 59.3 to 78.1 mW/cm^2. In the oxalic acid case, the reaction resistance decreased from 0.197 to 0.170 Ω cm^2 and peak power density increased from 69.7 to 85.8 mW/cm^2. These results show that the catalytic

activities of these cells were improved by the anodic treatment when acetic and oxalic acids were employed despite the IR resistance increase. It is suggested that the improved performance and reduced reaction resistance might have come from the formation of Ru hydrous oxide as shown in the sulfuric acid case [19]. In the formic and citric acid treated cells, only slight changes were observed in the reaction resistances and the peak power densities, meaning that these two acids are not suitable for anodic treatment at the condition of this work. Note that the reaction resistance cannot be directly correlated to the peak power value, because the reaction resistance values were measured at a certain applied current density of 100 mA/cm^2 and IR resistance also affects the performance of single cells.

Here, we discuss why the anodic treatment results are dependent on the acid solutions. One of the effective factors might be pH of acid solutions, because pH is a key parameter that determines the oxide form of Ru. As mentioned above, the anodic treatment enhances the MOR activity by changing the surface properties of Ru; therefore, the pH of the acid solution can affect the results. As mentioned above, ideal pH values of each acid solution (1 M) are 1.9, 2.4, 1.8, 3.6 and 0 for the formic, acetic, oxalic, citric and sulfuric acids, respectively. The order of performance improvement was 'sulfuric acid>acetic acid>oxalic acid>formic acid>citric acid', while the order of pH is 'sulfuric acid<oxalic acid<formic acid<acetic acid<citric acid'. Thus, pH and performance improvement could not be correlated directly. Another possibility is an electrochemical oxidation of organic acids by the catalyst during the anodic treatment. For example, formic acid is widely studied as an alternative liquid fuel to replace methanol [29]. Electrochemical reactivity of the PtRu catalyst with the acid solutions was tested by using a half-cell set-up. Linear sweep voltammetry results are shown in Fig. 4, where an increase of current density by electrochemical oxidation was observed only for the formic acid solution. This result means that formic acid is not applicable as an anodic treatment medium despite its low pH. The other acid solutions did not exhibit electrochemical oxidation up to 0.5 V during the linear sweep voltammetry testing. For the citric acid case, high pH might be the reason for its poor performance for the anodic treatment, which means a certain range of pH is necessary to tune the surface properties of Ru at 0.7 V (potential employed for the anodic treatment in this study). It is still
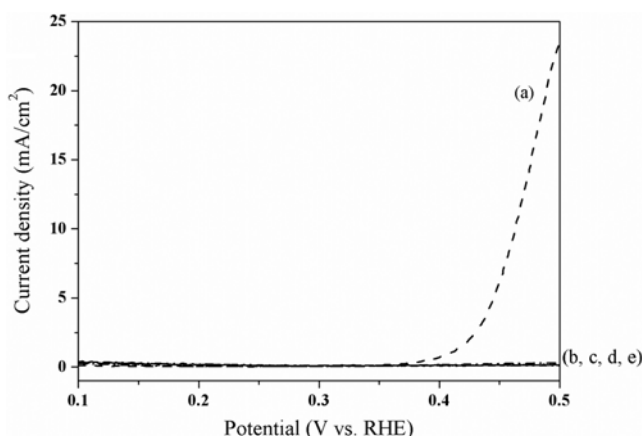
Fig. 4. The linear sweep voltammetry results performed for various electrolyte solutions which contains 1 M H$_2$SO$_4$ and 1 M of (a) formic acid, (b) acetic acid, (c) oxalic acid, or (d) citric acid, respectively. 1 M H$_2$SO$_4$ solution without organic acids was also tested for comparison purpose and shown as (e).

feasible that citric acid can work at higher potentials, but it should be considered that applying higher potential can cause serious damage against the catalyst layers such as catalyst particle agglomeration and dissolution of Ru.

CONCLUSIONS

Four acidic solutions were employed for the anodic treatment of DMFCs, and 32 and 23% improvement in the peak current densities was achieved when acetic and oxalic acids were employed, respectively. On the other hand, no improvement was observed when formic and citric acids were used. The EIS simulation results confirmed that catalytic activities of the single cells were improved after the anodic treatment for the acetic and oxalic acid cases; the reaction resistance of each single cell decreased by 0.029 and 0.027 Ω cm^2 for the acetic and oxalic acid solutions, respectively, while it decreased by 0.003 and 0.005 Ω cm^2 for the formic and citric acid solutions, respectively. However, it was observed that oxalic acid has negative effects on the IR resistance components. Therefore, it could be concluded that oxalic acid can be employed as an alternative to sulfuric acid in the anodic treatment process for the conditions of this study.

ACKNOWLEDGEMENTS

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