

# Electrochemical behavior of A356 Al alloy and its vortex and squeeze composites containing ZrO<sub>2</sub> in 3.5 % NaCl solution

Awad Sadek Mogoda (✉ [awad.sadek@cu.edu.eg](mailto:awad.sadek@cu.edu.eg))

Cairo University Faculty of Science <https://orcid.org/0000-0001-8965-7452>

Khaled M Zohdy

Higher Technological Institute

Mohamed Ali Aboutabl

Cairo University Faculty of Science

---

## Research Article

**Keywords:** A356 Al/ZrO<sub>2</sub> composites, 3.5% NaCl, Polarization, EIS, SEM, EDS

**Posted Date:** March 19th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-322109/v1>

**License:**   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

# Abstract

Corrosion of A356 Al alloy and its composites reinforced by  $ZrO_2$  and prepared by vortex and squeeze casting was studied in 3.5 % NaCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results of polarization and EIS indicated that the corrosion resistance of the vortex cast composites increases with the increasing in the vol. % of  $ZrO_2$  up to 20 % then decreases again at 30 % in the chloride solution. Also, the corrosion resistance of the squeeze cast composites increases as the squeeze pressure increases due to decreasing the porosity within these composites. Additionally, the SEM micrographs well-showed that the defects and notches which appeared on the surface of the mechanically polished vortex cast composite were diminished due to growth of a protective passive film on the composite in the chloride solution. Also, the squeeze cast composite is covered by a thick passive film and less exposure to corrosion in comparing with surface of the vortex cast composite. Energy dispersive spectroscopy (EDS) spectra found out the presence of a passive aluminium oxide layer on the A356 Al alloy/ $ZrO_2$  composites.

## 1. Introduction

Al-Si alloys are attractive materials for use in aerospace and automotive industries due to their light weight, high specific strength, corrosion resistance, modulus, and high thermal conductivity. Metal matrix composites (MMCs) are preferred among the new engineering materials, where a strong ceramic reinforcement is incorporated into the metal matrix to improve its properties, including the specific strength, specific stiffness, corrosion resistance, wear resistance, and modulus [1,2]. Particle-reinforced metal matrix composites are important materials for use in aerospace, automotive and tribological applications because of their higher specific strength and high specific stiffness at room and elevated temperatures. Aluminium alloy matrix composites (AMC) reinforced with ceramic particles acquire good mechanical properties than unreinforced aluminium alloy [3].

Reinforcing the Al matrix alloy with  $ZrO_2$  particles increased the hardness and ultimate tensile strength of the alloy produced with 15 vol. % of  $ZrO_2$  at 750 °C to the maximum values of 70 BHN and 232 MPa [4]. The addition of alumina ( $Al_2O_3$ ), titanium dioxide ( $TiO_2$ ) and zirconia ( $ZrO_2$ ) nanoparticles as reinforcement agents to the cast A 356 Al alloy as a base metal matrix enhanced its mechanical properties [5]. Reinforcing the A356 Al alloy matrix composite with  $ZrO_2$  resulted in increase of the composite hardness with increasing of the zirconia content and improves the tribological property of the material [6].

Erosive-corrosive wear behavior of A 356 Al alloy and its composite reinforced by  $ZrO_2$  and produced by vortex and squeeze techniques in water containing 40% sand slurry revealed found that the squeezed cast composite is characterized by high corrosion and wear resistances comparing the vortex cast composite [7]. The corrosion behavior of aluminium matrix nanocomposites of an aluminium alloy Al 6061 reinforced with different percentages of n- $ZrO_2$  (2.5, 5 and 7.5 wt. %) in 3.5 % NaCl showed that

corrosion rate decreases as the concentration of zirconia increases and the reinforced aluminum alloy with 7.5 wt. % has lower corrosion rate than other composites [8]. Corrosion study of Al 7075, Al 2024, and Al 6061 in the Red Sea water showed that the corrosion rate decreases continually as the time of exposing to the corrosive medium increases but the increase of temperature led to increase in the anodic and cathodic current density and a decrease in the corrosion potential [9]. It is clear from the previous literature that real work was done on A356 Al alloy and its composites containing  $ZrO_2$  in NaCl solution, therefore the aim of the present work is to study the effects of zirconia content and the squeeze pressure of A356 Al/  $ZrO_2$  composites on their electrochemical behavior in 3.5 % sodium chloride solution. Potentiodynamic polarization and electrochemical impedance spectroscopy have been used for the present study. The surface morphology of the tested materials were investigated using scanning electron microscopy (SEM) and energy dispersive X-ray (EDS).

## 2. Experimental

### 2.1. Materials

A356 Al alloy with chemical composition (wt. %) 6.6 Si, 0.5 Fe, 0.34 Cu, 1 Mg and rest Al was used as the matrix alloy. Vortex cast composites were prepared by dispersing different vol. % of  $ZrO_2$  particles with size of 40-100  $\mu\text{m}$  in the matrix alloy using vortex technique. The composite with 5 %  $ZrO_2$  was solidified in a permanent mold using a squeeze casting technique under different pressures namely 20, 50, and 88 MPa [7].

Prior to immersion in the acid rain, the electrodes of test composites were abraded using successively grades emery papers down to 2000 grit, then rubbed with a soft cloth until they acquired a mirror-bright surface and rinsed with distilled water. Analar grade sodium chloride was used. The measurements have been achieved in stagnant solutions at 25 °C.

### 2.2. Electrochemical tests

EIS and potentiodynamic polarization measurements were conducted using the electrochemical workstation 1M6e zahner elektrik (GmbH, Meßtechnik, Kronach, Germany) [10, 11]. The Echem Analyst software (version 5.21) was used for the electrochemical data analysis. The electrolytic cell was a glass double-jacket three electrode cell. A platinum metal was used as an auxiliary electrode. All potential were measured and reported against saturated calomel electrode (SCE) as a reference electrode. The EIS measurements were performed at open circuit potential. The input signal was usually 10 mV peak to peak in the frequency range from 0.01 Hz to  $10^5$  Hz. Potentiodynamic scans were traced from -1.5 to +0.2 V vs. SCE at a rate of  $1 \text{ mV s}^{-1}$ .

### 2.3. Characterization

The surface morphologies of test electrodes were observed by scanning electron microscopy (SEM, Quanta 250 FEG, FEI company, Netherlands). The chemical analysis of electrode surface was performed

by energy dispersive X-ray spectroscopy (EDS, X Flash detector 4010, Bruker, Germany).

## 3. Results And Discussion

### 3.1. Effect of zirconia content of A 356 Al alloy/ZrO<sub>2</sub> composites on their corrosion in 3.5 % NaCl solution

#### 3.1.1. Potentiodynamic polarization measurements

The polarization curves of A 356 Al alloy and its vortex cast composites containing different vol. % of ZrO<sub>2</sub> in 3.5 % sodium chloride solution are shown in Figure 1. The cathodic and anodic curves of the studied materials are similar i.e., they exhibit the same anodic and cathodic processes. The corrosion parameters which are the corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), corrosion rate in mpy, slope of the cathodic branch ( $\beta_c$ ) and slope of the anodic branch ( $\beta_a$ ) were estimated and listed in Table 1.

The value of the corrosion potential tends to increase as the zirconia content of the composites increases up to a maximum value at 20 vol. % and then decreases at 30 vol. % as shown in Table 1. This shift in the value of  $E_{\text{corr}}$  to the noble value conforms a decrease in the corrosion rate of the composites as the vol. % of ZrO<sub>2</sub> increases. It has been found in the literature [8] that the corrosion potential of the Al-6061 composites in 3.5 % NaCl solution increases with increasing the weight percentage of zirconia in the composites which attributed to the decrease in the corrosion rate.

Also, it can be seen from Table 1 that the value of  $I_{\text{corr}}$  decreases and consequently the corrosion rate decreases as zirconia content in the composites increases in a manner like that of the corrosion potential behavior. This may be due to the formation of a protective layer of corrosion products, consist mainly of less soluble aluminium compounds in sodium chloride solution [9]. Figure 2a and b shows the SEM micrographs for the vortex cast composite containing 5 % ZrO<sub>2</sub> after the mechanically polishing of its surface and after immersion it in 3.5 % NaCl for 10 days, respectively. It is clear that the defects and notches which appear in Figure 2a were decreased due to growth of a protective passive film on the composite surface in the chloride solution as shown in Figure 2b.

Also, the results of the EDS analysis shown in Figure 3a and b for the surface of mechanically polished vortex cast composite (3a) and for the same surface after immersion it in sodium chloride solution for 10 days (3b) reveal that the passive film formed on these surfaces consists mainly of aluminium oxide layer.

#### 3.1.2. Electrochemical impedance measurements

The EIS spectra have been recorded for the unreinforced A 356 Al alloy and its vortex cast composites containing different percentages namely 5, 20, and 30 vol. % of ZrO<sub>2</sub> in the chloride solution at open-circuit potential. The results are shown in Figure 4 as Nyquist plots which are a part of the imperfect capacitive semicircles due to the frequency dispersion [12]. The capacitive semicircle increases in

diameter with increasing the percentage of ZrO<sub>2</sub> added to A 356 Al alloy up to 20% then decreases again slightly at 30%. This means that the corrosion resistance of vortex cast composites surfaces in the chloride solution increases as ZrO<sub>2</sub> concentration increases to 20 % then decrease.

The impedance data were analyzed using the equivalent electrical circuit (EEC) in Figure 5. This circuit is similar to that used before in our work on titanium in NaF solutions [10]. The components of this EEC are as follows: R<sub>s</sub> solution resistance; C<sub>dl</sub> double layer capacitance; R<sub>ct</sub> charge transfer resistance that related to the corrosion process; C<sub>f</sub> capacitance due to the dielectric nature of the surface film and R<sub>f</sub> resistance due to the surface film.

Since there is a variance between real capacitance and pure capacitance therefore, computer simulation of the EIS spectra can be carried out by replacing the capacitance C, with a constant phase element (CPE). The impedance of CPE is described by the following expression [13,14]:

$$Z_{CPE} = [(j\omega)^{\alpha} Y]^{-1}$$

where Y is the frequency independent real constant of the CPE,  $\omega$  the angular frequency,  $j = \sqrt{-1}$ , and  $\alpha$  is an adjustable empirical exponent which varies between 1.0 for a perfect smooth surface with pure capacitive behavior and 0.5 for a porous surface.

The fitted EIS parameters for the tested materials in the sodium chloride solution were listed in Table 2. It is obvious from this Table that the R<sub>f</sub> increases and simultaneously C<sub>f</sub> decreases as the percentage of zirconia in the composites increases up to 20% then R<sub>f</sub> decrease and C<sub>f</sub> increases at 30%. These variations can be attributed to the increase of the thickness of primary passive film on these materials as the zirconia content increases to 20% and it decreases when this content equals 30%.

## **3.2. Effect of casting pressure of A 356 Al alloy/ 5 vol. % ZrO<sub>2</sub> composites on their corrosion in 3.5 % NaCl solution**

### **3.2.1. Potentiodynamic polarization measurements**

The polarization curves for the vortex and squeeze cast composites of A 356 Al alloy reinforced with 5 vol. % of ZrO<sub>2</sub> in 3.5 % sodium chloride solution are given in Figure 6. The squeeze composites cast under different pressures namely 20, 50 and 88 MPa. Figure 6 shows similar polarization curves and passivity characteristics for the vortex and squeeze cast composites. This means the same corrosion processes occur for the two types of composites tested here in the chloride solution.

The polarization parameters were listed in Table 3 in which E<sub>corr</sub> increases and corrosion rate decreases with increasing of the pressure used for the squeeze cast composites due to decreasing of their porosity. Also, the values of the corrosion rate for the squeeze composites are lower than that for vortex cast composite of the same percentage of zirconia. Previously, it was found that the values of corrosion current density for A 356-10 vol. % SiC composite cast by gravity are greater than those for composite

cast by squeeze in 0.05 and 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions [15]. Therefore in sodium chloride solution the squeeze cast composite is less exposure for the corrosion process than the vortex one because of the lower porosity content of squeeze one.

Figure 7a and b shows the SEM micrographs for the mechanically polished surfaces of the vortex cast composite (7a) and squeeze cast composite at 50 MPa (7b) before immersion in the chloride solution. It is obvious from this Figure that the pores of different sizes spread in large amount on the surface of vortex cast composite than on the surface squeeze one. Many researchers had been found that the percentage of porosity for the squeeze composite decreases with the increase in the pressure during the preparation process [7, 15-17].

### 3.2.2. Electrochemical impedance measurements

The EIS results for the vertex and squeeze cast composites containing 5 vol. % of ZrO<sub>2</sub> in 3.5 % NaCl solution are given in Figure 8 as Nyquist plots. The diameter of the capacitive semicircle increases as the squeeze pressure increases due to increase of corrosion resistance. Fitting of EIS results were carried out using the EEC in Figure 5 and the results are given in Table 4. Both the charge transfer resistance, R<sub>ct</sub>, and passive film resistance, R<sub>f</sub>, increase as the pressure of squeeze cast composites increases and they are being greater than those of vortex composite. This means that the increases of casting pressure of the composite from 20 to 88 MPa leads to a decrease of the porosity within the composite and consequently results in formation of more passive film on its surface.

Figure 9a and b shows the SEM photographs for the surfaces of the vortex and squeeze cast composites after immersion in sodium chloride solution for 10 days. From this Figure it can be seen that the repairing of the surface due to growth the pre-immersion passive film in case of squeeze composite is good than in the case of vortex one which is consistent with the polarization and EIS results.

## 4. Conclusion

The polarization and EIS results of A 356 Al alloy/ZrO<sub>2</sub> vortex cast composites in 3.5 % NaCl solution indicate that the corrosion resistance of the composites increases with the increase of the zirconia content in these materials due to formation of a protective layer of aluminium compound on the composites. Also, the obtained results of polarization and EIS for A 356 Al alloy/ZrO<sub>2</sub> squeeze cast composites in the chloride solution revealed that the corrosion resistance of these composites increases as the squeeze pressure increases due to decreasing the porosity within the composites. The SEM micrograph for the mechanically polished composite surface showed that the chloride solution assists in repairing and growth the air formed film on this material. The surface of the squeeze cast composite contains less porosity than the vortex composite and leads to formation a more protective film on the squeeze one.

## References

1. P.Davima, J. Silva and A.M.Baptista, *J. Mater.Process.Technol.*, 183 (2007) 358.
2. Kok, *J. Mater.Process.Technol.*, 161 (2005) 381.
3. Kok and K. J. Ozdin, *J. Mater. Process. Technol.*, 183 (2007) 301.
4. Abdizadeh and M.A. Baghchesara, *Mechan. Compos. Mater.*, 49 (2013) 571.
5. S. El-Mahallawi, A. Y. Shash and A.E. Amer, *Metals*, 5 (2015) 802.
6. Mariyappan, P. Sarangapani, G. Perumal and A. Sathiyamoorthi, *Compos. J. Chem. Pharmaceu. Sci.*, 9 (2015) 98.
7. T. A. El-Khair and A. A. Aal, *Mater. Sci. Eng., A* 454 (2007) 156.
8. Ramachandra, G. D. Maruthi, and R. Rashmi, *Inter. J. Mater. Metall. Eng.*, 10 (2016) 1321.
9. H. Al-Moubaraki and H. H. Al-Rushud, *Int. J. Corros.*, (2018).
10. S. Mogoda and K. M. Zohdy, *Int. J. Electrochem. Sci.*, 15 (2020) 8070.
11. S.Mogoda, *Bull. Mater. Sci.*, 43 (2020)100.
12. Lebrini, M. Lagrenee, H. Vezin, M. Traisnel and F. Bentiss, *Corros. Sci.* 49 (2007) 2254.
13. Juttner, *Electrochim. Acta*, 35 (1990)1501.
14. E. Heakal, A. A. Ghoneim, A. S. Mogoda and Kh.Awad, *Corros. Sci.*, 53 (2011) 2728.
15. Fattah-Alhosseini, M. Ranjbaran, and S. Vajdi Vahid, *Int. J. Corros.*, ( 2014).
16. T. A. El-Khair, *Mater. Lett.*, 59 (2005) 894.
17. T. A. El-Khair, *Int. J. Eng. Res. Africa*, 4 (2011) 59.

## Tables

Table 1: Potentiodynamic polarization results for A356 Al alloy and its vortex cast composites with different vol. % of ZrO<sub>2</sub> in 3.5 % NaCl solution.

Vol. % ZrO <sub>2</sub>	E <sub>corr</sub> mV	I <sub>corr</sub> μA/cm <sup>2</sup>	B <sub>a</sub> mV/decade	β <sub>c</sub> mV/decade	Corrosion rate mpy
0	-677	26.30	153	189	21.25
5	-587	3.48	437	470	2.810
20	-545	2.00	494	276	1.619
30	-557	2.54	219	388	2.053

Table 2: Characteristic parameters for fitting the experimental EIS results for A356 Al alloy and its vortex cast composites with different vol. % of ZrO<sub>2</sub> in 3.5 % NaCl solution.

Vol. % ZrO <sub>2</sub>	R <sub>s</sub>	R <sub>ct</sub>	C <sub>dl</sub>		R <sub>f</sub>	C <sub>f</sub>	
	Ω	Ω cm <sup>2</sup>	μF cm <sup>-2</sup>	α <sub>1</sub>	Ω cm <sup>2</sup>	μF cm <sup>-2</sup>	α <sub>1</sub>
0	22.57	378	3.12	0.84	8085	6.19	0.76
5	16.12	402	3.03	0.89	9130	5.51	0.81
20	21.30	450	2.79	0.85	13000	3.71	0.73
30	35.65	430	2.93	0.91	11990	4.34	0.80

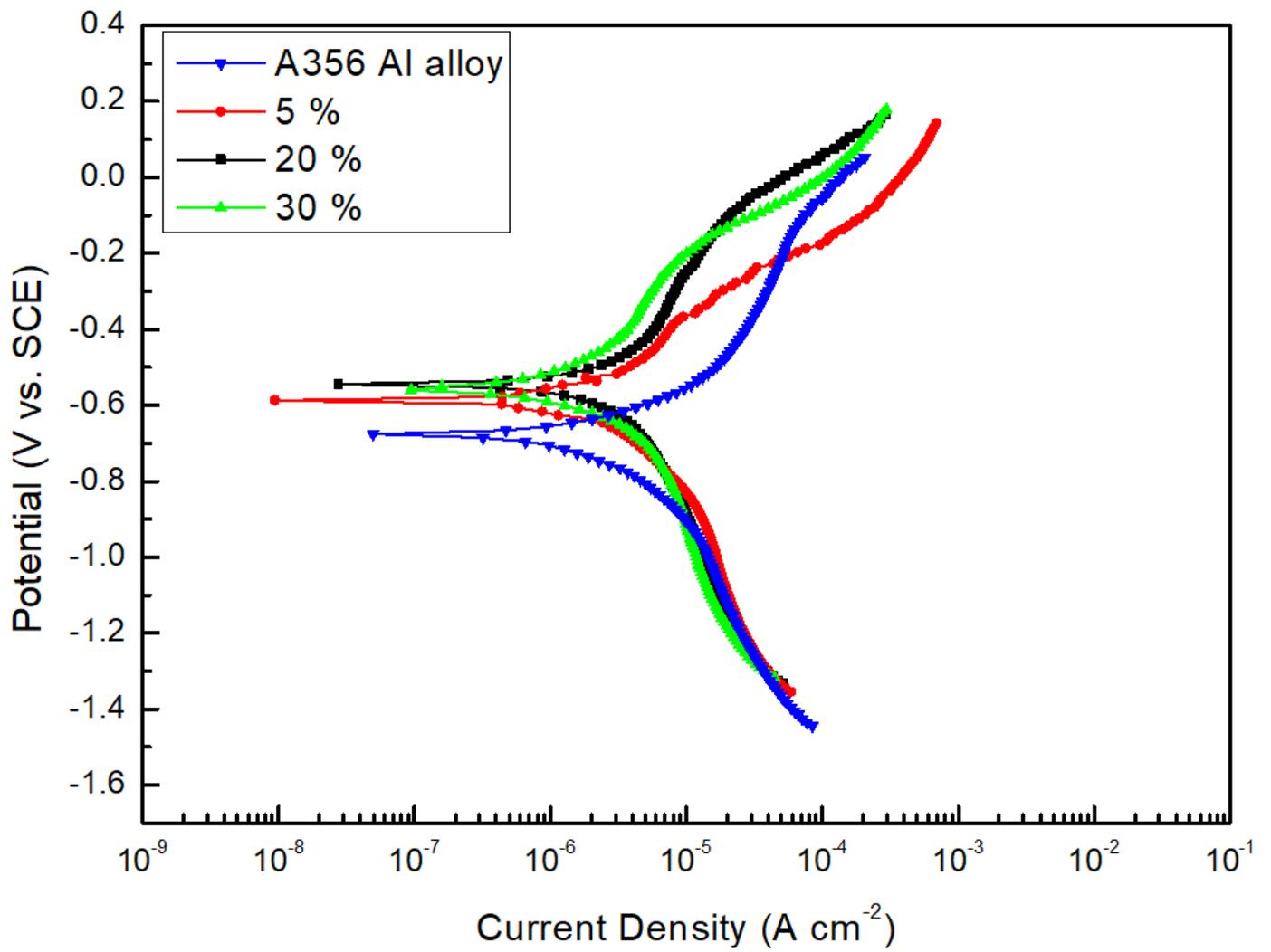
Table 3: Potentiodynamic polarization results for vortex and squeeze cast composites (at different squeeze pressures) in 3.5 % NaCl solution.

Squeeze pressure MPa	E <sub>corr</sub> mV	I <sub>corr</sub> μA/cm <sup>2</sup>	Ba mV/decade	Bc mV/decade	Corrosion rate mpy
Vortex cast	-587	3.48	437	470	2.809
20	-560	1.600	64	251	1.293
50	-538	1.210	53	173	0.977
88	-490	0.546	43	182	0.440

Table 4: Characteristic parameters for fitting the experimental EIS results for vortex and squeeze cast composites (at different squeeze pressures) in 3.5 % NaCl solution.

squeeze pressure MPa	R <sub>s</sub>	R <sub>ct</sub>	C <sub>dl</sub>		R <sub>f</sub>	C <sub>f</sub>	
	Ω	Ω cm <sup>2</sup>	μF cm <sup>-2</sup>	α <sub>1</sub>	Ω cm <sup>2</sup>	μF cm <sup>-2</sup>	α <sub>1</sub>
Vortex cast	16.12	402	3.03	0.89	9130	5.51	0.81
20	18.85	534	2.69	0.86	12330	4.76	0.76
50	15.86	676	2.32	0.91	12700	4.46	0.81
88	21.30	780	2.21	0.88	13000	3.71	0.74

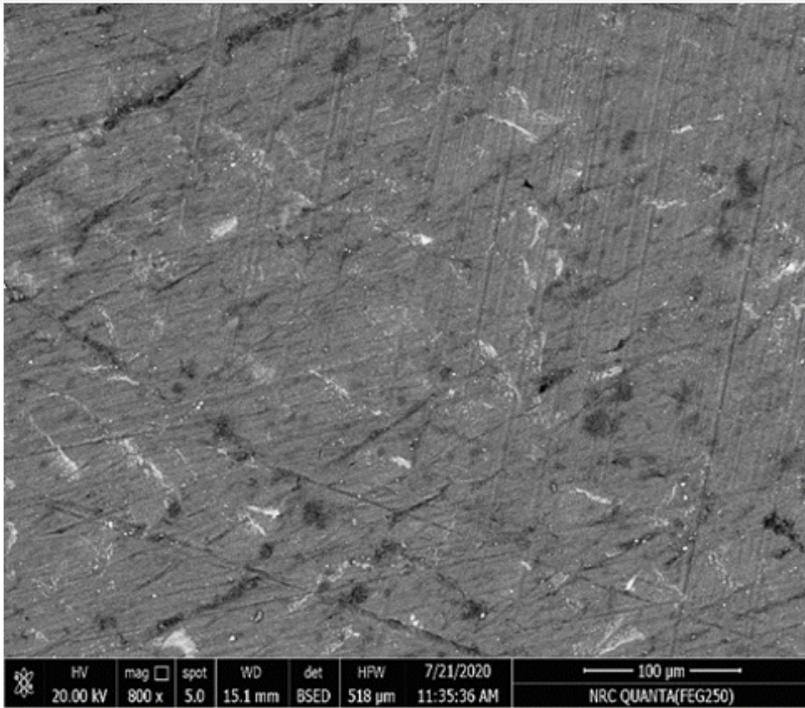
## Figures



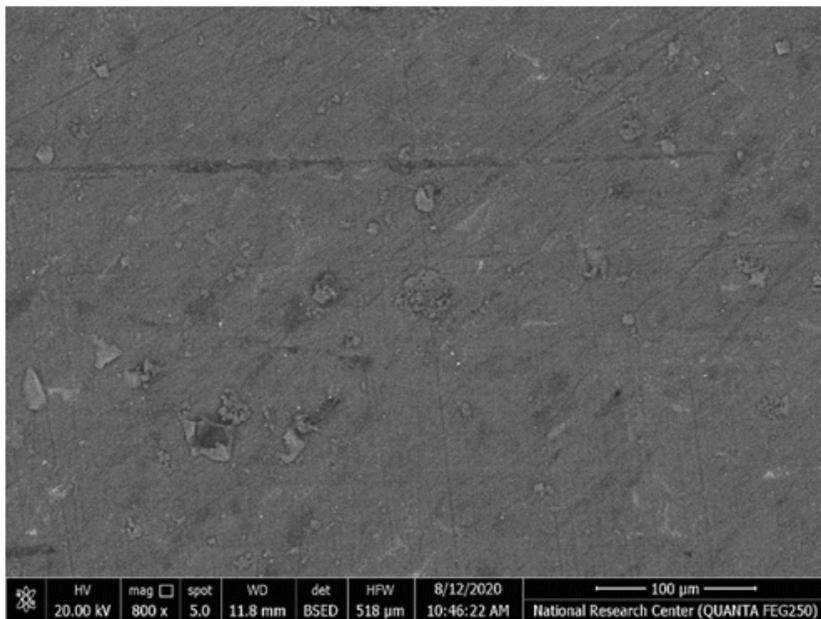
**Figure 1**

Potentiodynamic polarization curves for A356 Al alloy and its vortex cast composites with different vol. % of ZrO<sub>2</sub> in 3.5 % NaCl solution.

a

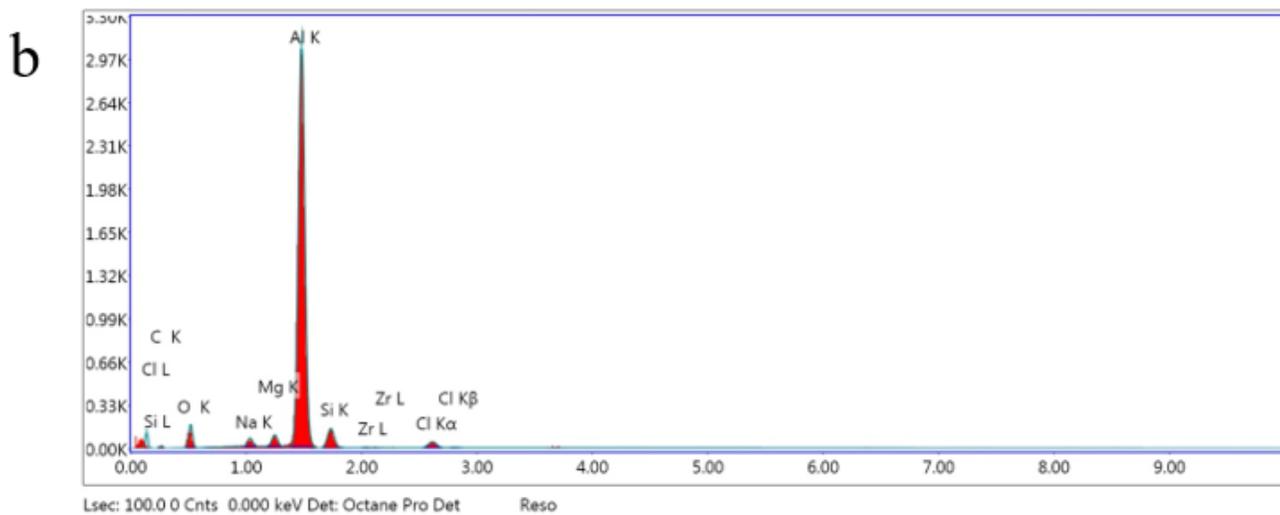
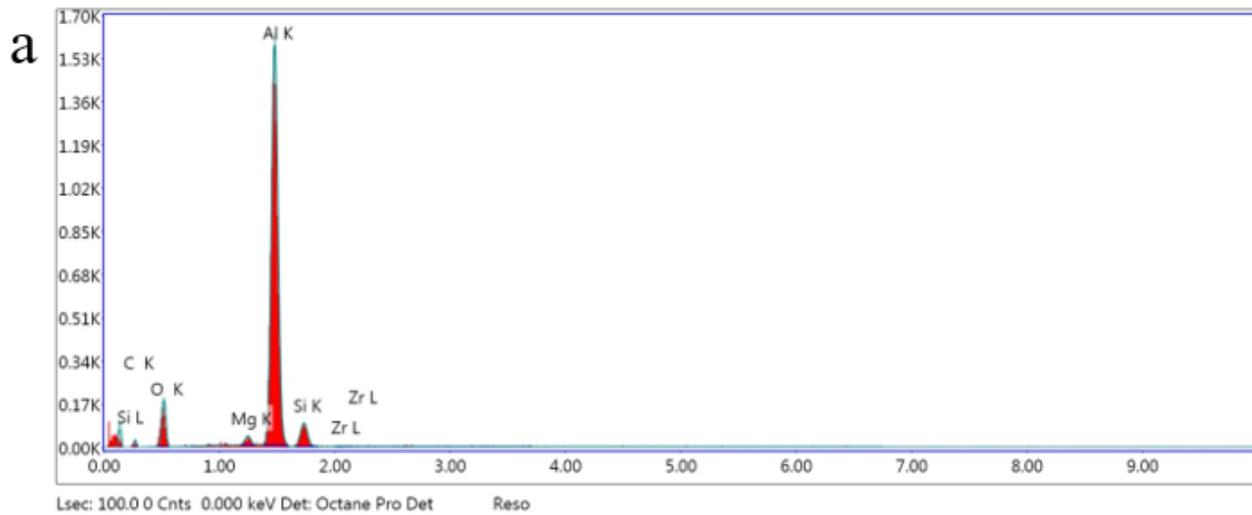


b



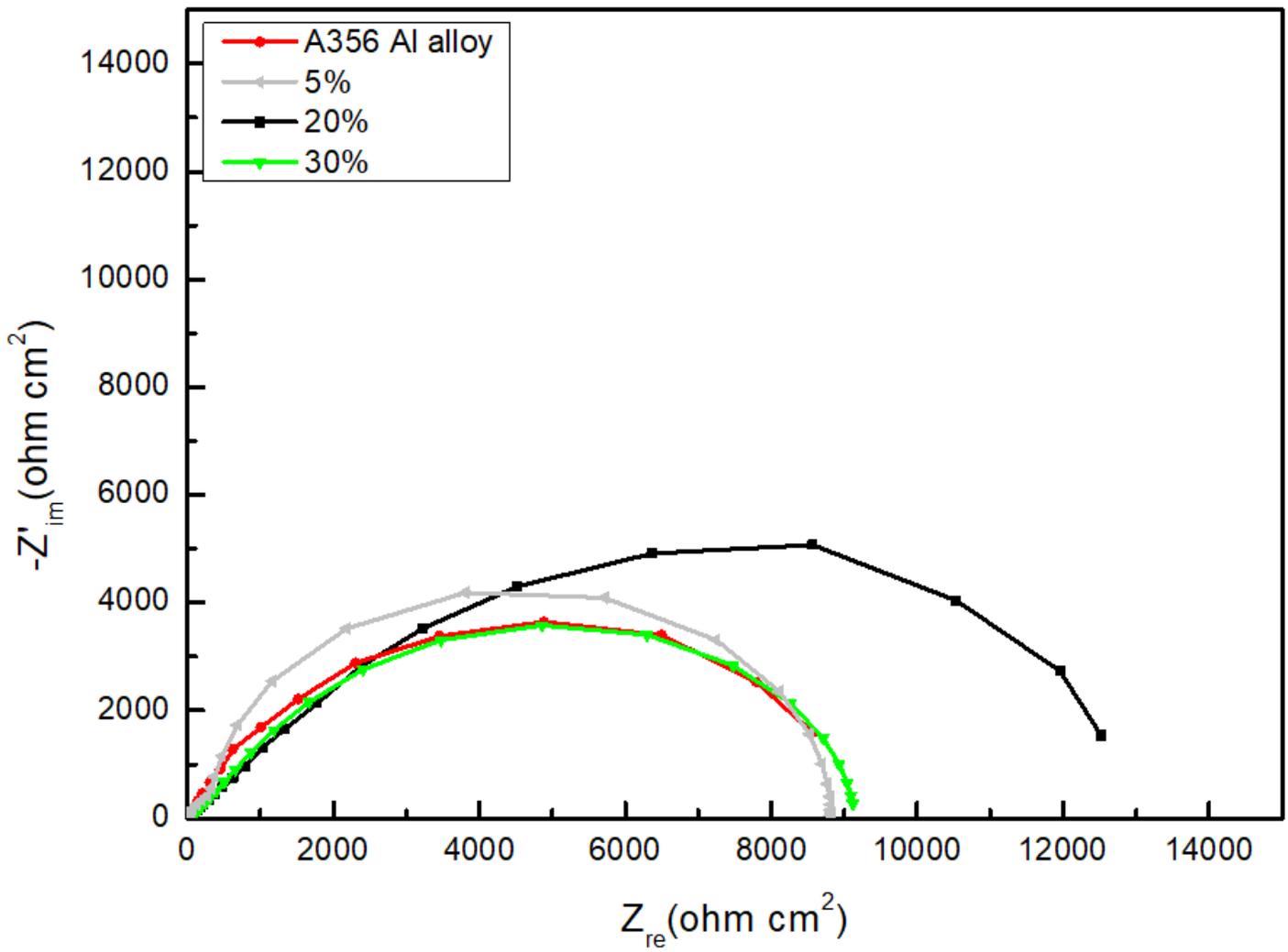
**Figure 2**

SEM micrographs for the surfaces of vortex cast composite contains 5 % zirconia (a) after mechanically polishing and (b) after immersion for 10 days in 3.5 % NaCl solution.



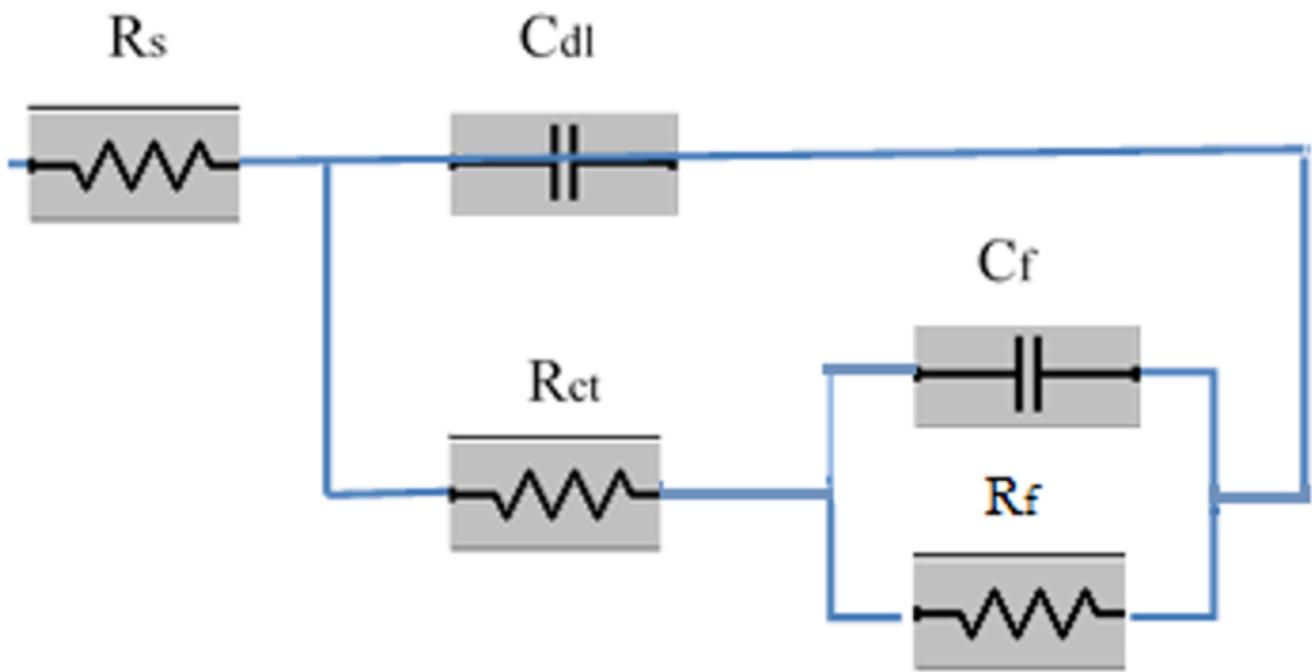
**Figure 3**

EDS analysis for the surfaces of vortex cast composite contains 5 % zirconia (a) after mechanically polishing and (b) after immersion for 10 days in 3.5 % NaCl solution.



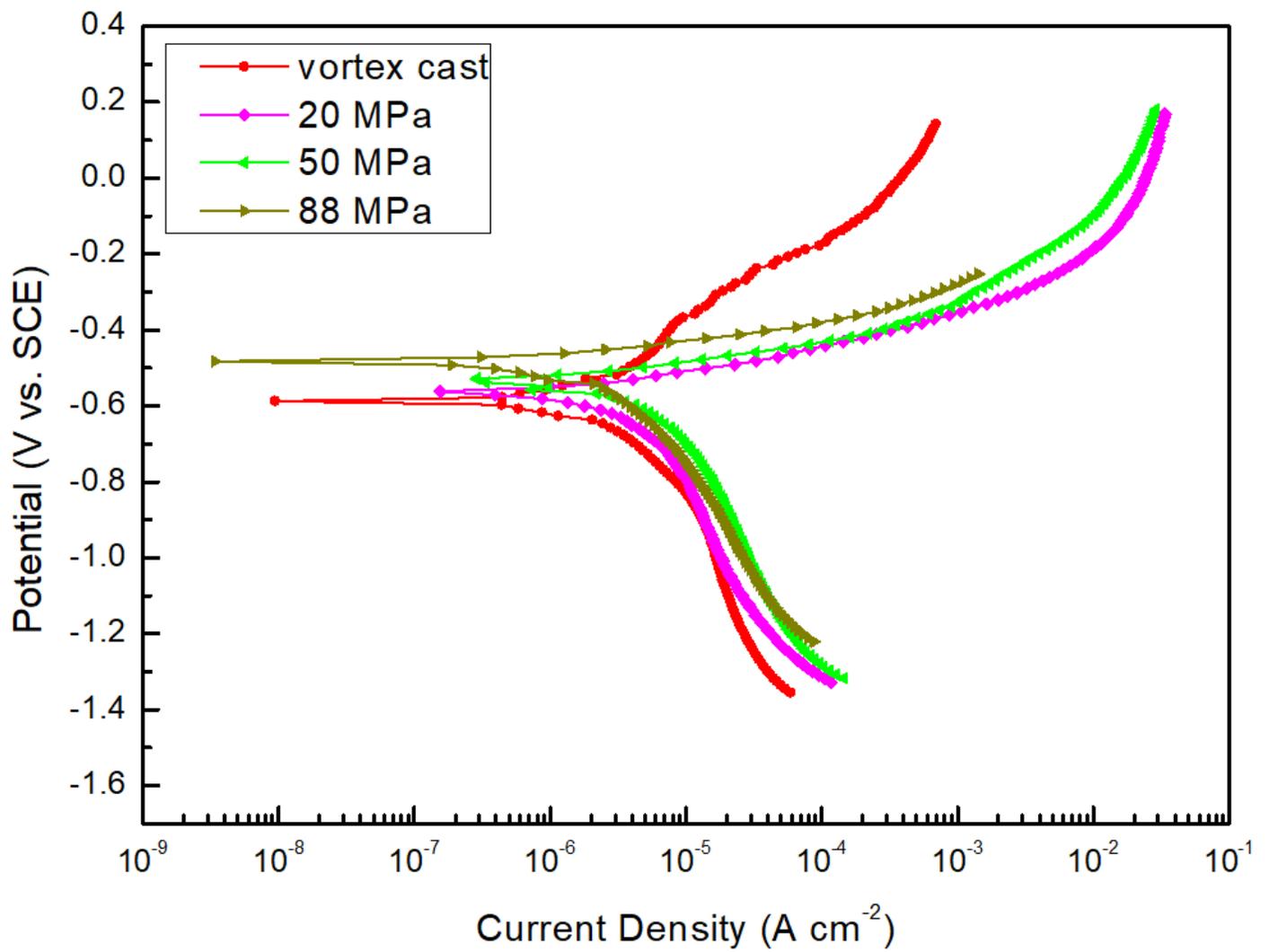
**Figure 4**

Nyquist plots for A356 Al alloy and its vortex cast composites with different vol. % of ZrO<sub>2</sub> in 3.5 % NaCl solution.



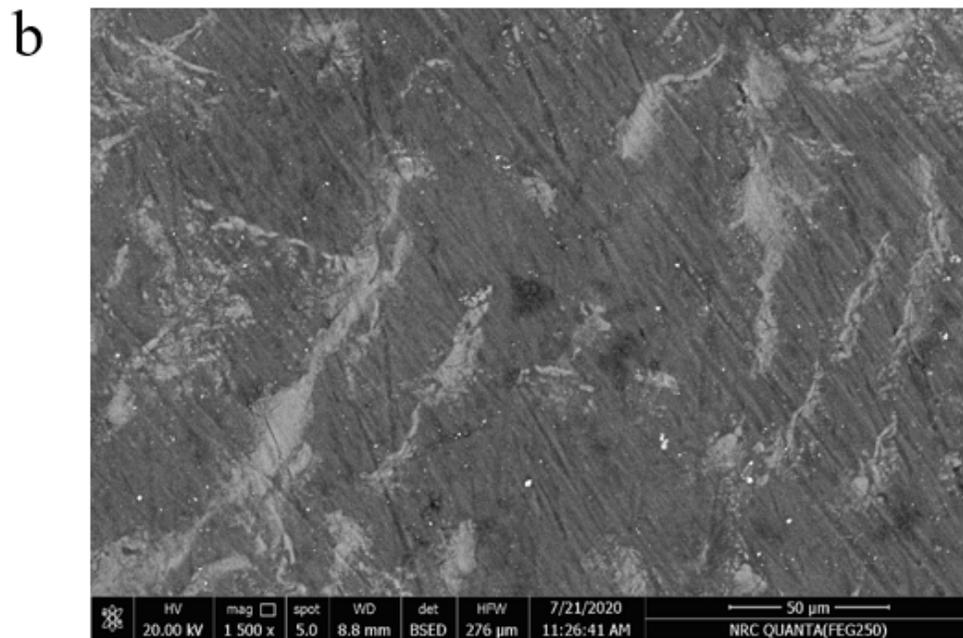
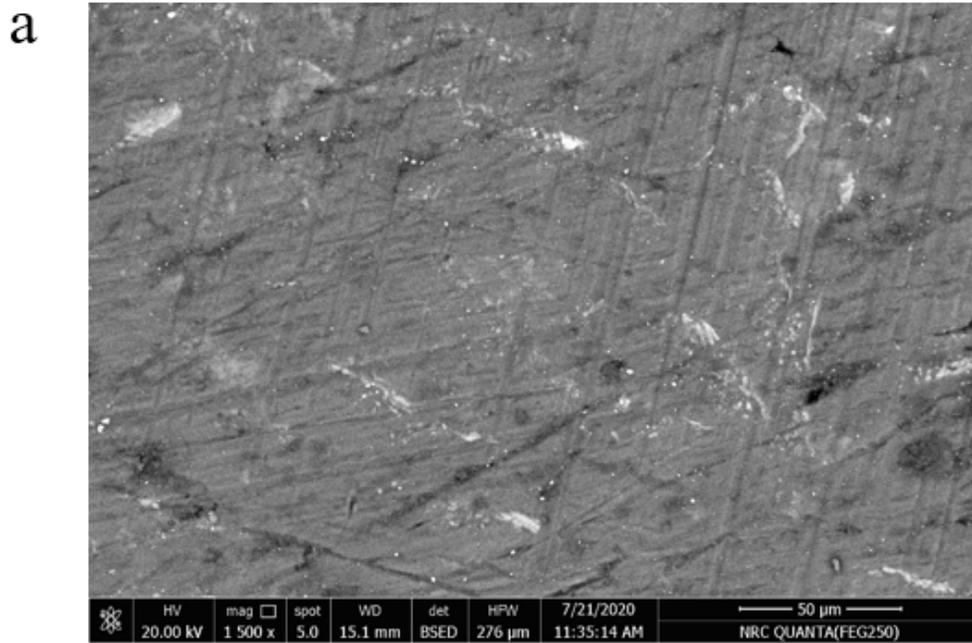
**Figure 5**

Equivalent electrical circuit for fitting the impedance data for A356 Al alloy and its vortex and squeeze cast composites in 3.5 % NaCl solution.



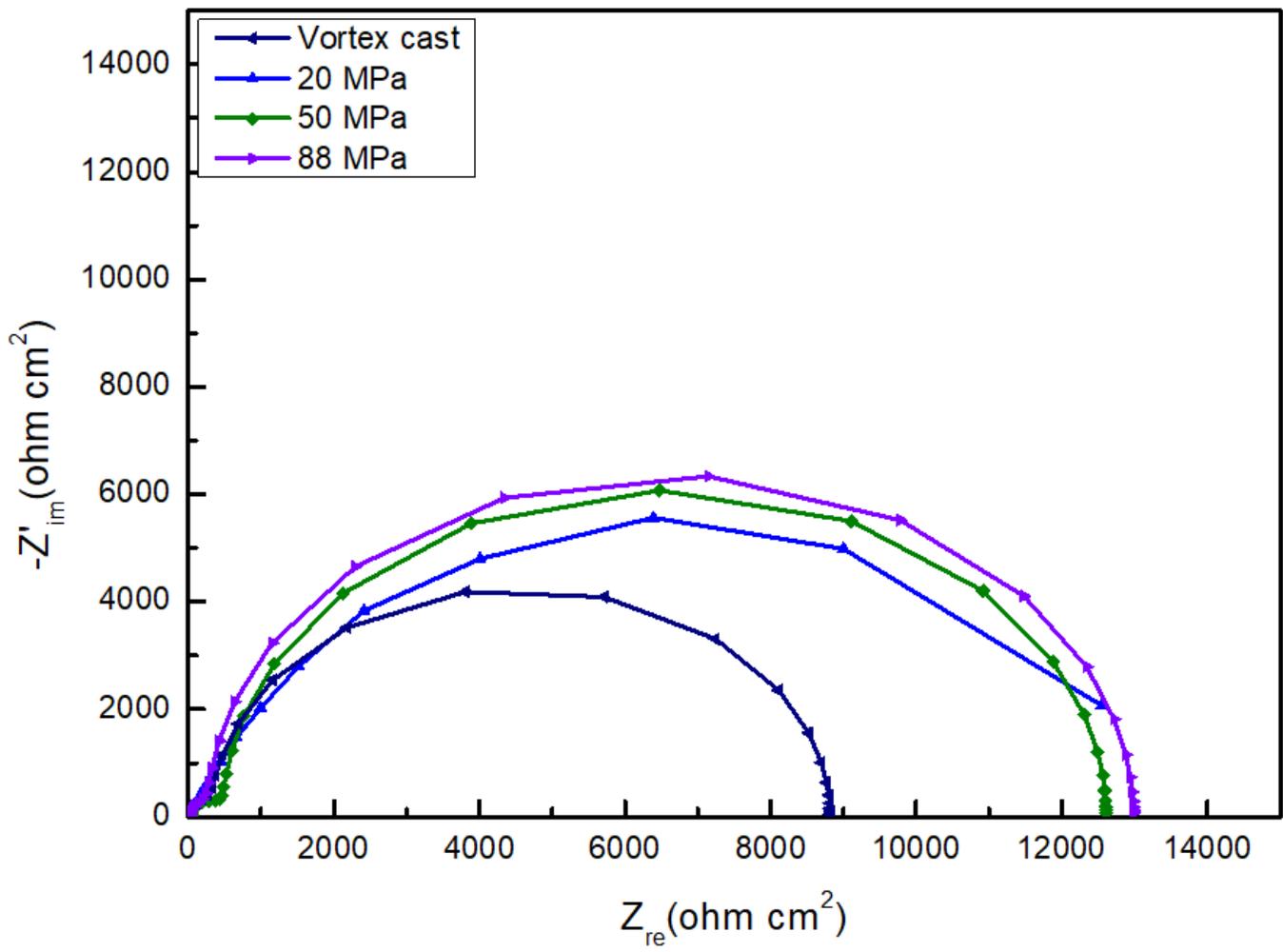
**Figure 6**

Potentiodynamic polarization curves for vortex and squeeze cast composites (at different squeeze pressures) in 3.5 % NaCl solution.



**Figure 7**

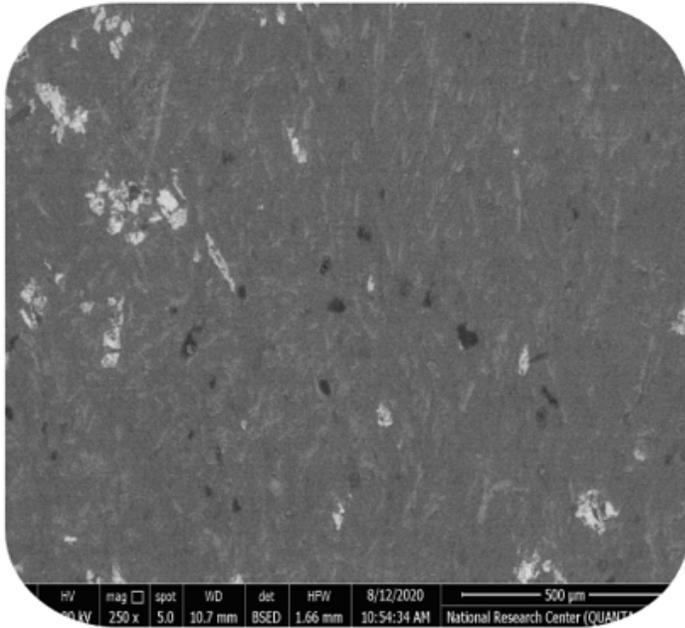
SEM micrographs for the mechanically polished surfaces of the (a) vortex cast composite and (b) squeeze cast composite at 50 MPa before immersion in the chloride solution.



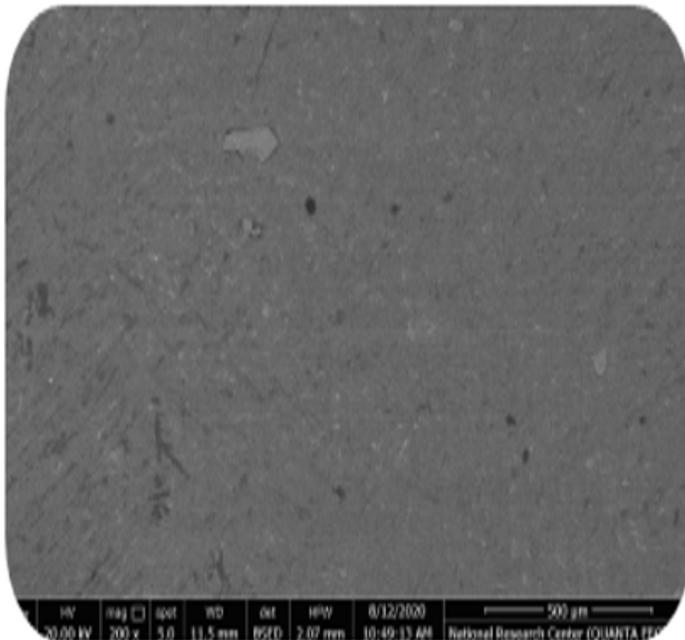
**Figure 8**

Nyquist plots for vortex and squeeze cast composites (at different squeeze pressures) in 3.5 % NaCl solution.

a



b



**Figure 9**

SEM micrographs for the surfaces of (a) vortex and (b) squeeze cast composites after immersion for 10 days in 3.5 % NaCl solution.