

The Effect of Electrolyte Ingredients on Electrolyte-Electrode Interface in Electrocoating: A Comparative Study

Hacer Dolas¹, Keziban Huner² and A.Sezai Sarac^{3*}

1. Program of Occupational Health and Safety, Hilvan Vocational School, Harran University, 63900, Sanliurfa, Turkey
2. Department of Chemistry, Yildiz Technical University, 34349, Davutpasa, Istanbul, Turkey
3. Department of Chemistry and Polymer Science & Technology, Istanbul Technical University, 34467, Maslak, Istanbul, Turkey

Corresponding author: sarac@itu.edu.tr

Abstract

In this study, CFs were coated electrochemically with three different monomers (An, EDOT or Py) in different condition such as electrolyte (BA, H₂SO₄ or NaClO₄), solvent (H₂O as inorganic medium or ACN as organic medium), in presence of foreign material (EBC) and coating method (constant potential and cyclic voltammetry as controlled potential). Obtained CFs were compared with regard to electrical and capacitive and morphological features.

In CPE the current flow in system was changed in certain values for each monomer in presence of EBC. But this changing was more for Py than that for the other. In CV experiments, the oxidation potential was increased for PAN and PEDOT when it was decreased for Py. I_{max} values were changed for each polymer and conditions. According to Randles-Sevcik equation, the electrocoating redox processes in BA-H₂O were not controlled by diffusion under this conditions. But, all the redox processes carried out in NaClO₄-ACN electrolyte solution were controlled by diffusion for each polymer coated CFs. In presence of EBC it could be concluded that redox process was controlled by diffusion in BA-H₂O for PAN and in NaClO₄-ACN for PEDOT.

In presence of 1.8 % EBC. The C_{DL} value was decreased to 4 μF from 6 μF; to 0.7 μF from 1.5 μF; to 1 μF from 3 μF in BA-H₂O for Pan, PEDOT and PPy respectively. But, it was increased to 11.5 μF from 10.4 μF in NaClO₄-ACN for PEDOT. Phase angle was in the same trend.

The texture coatings were more compact in the presence of EBC in electrolyte solution than that of the absence of EBC for PPy coated CF. The relationship of between the radius of coating and the C_{DL} of the coated CF was proportional. Thus, it may be concluded that the C_{DL} and radius of coating were affected with the presence of different material/compound in electrolyte solution.

Keywords: PAN, PEDOT, PPy, presence of EBC, comparison, impedance, texture coating.

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1. Introduction

Carbon fibers (CFs) have properties such as high strength and modulus, good stiffness, and creep resistance etc. For this reason, they have been used as the reinforcing material in the high performance resin composites which have been extensively used in a variety of areas such as the aerospace industry, automobile applications and sporting goods (Montes-Moran *et.al.* 2004).

Fibers and a matrix material (polymer resin) make interactively a new combination. One of the major advantages of the **fiber/resin** combination is its complementary nature. Others are that numerous method such as the electrochemical oxidation (Yue *et.al.* 1999; Gulyas *et. al.* 2001 & Febo *et. al.* 2002), plasma treatment (Montes-Moran *et.al.* 2001; Dilsiz *et.al.* 1995 & Bubert *et.al.* 2002), radiation treatment (Li *et.al.* 2005 & Xu *et.al.* 2007) methods, etc., have been used to treat the CFs surface in order to improve the interfacial performance between fiber and matrix.

In addition to the different methods, electrocoating with thin conductive polymer film is proposed by our group as feasible approach to add functionality onto the carbon fiber surface covalently (Kumru *et.al.* 2001). The film thickness, morphology and functionality of the formed coating can be precisely controlled with electrochemical coating method using following parameters i.e., current density, potential, monomer concentration, and scan rate etc. (Sarac *et.al.* 2008; Dolas & Sarac 2012).

Some polymers show conductive feature. This information is not known by the time the discovery of a polyacetylene (PA) thanks to that Shirakawa *et.al.* (1977) reported about conducting concept in the polymer.

These polymers have conjugation structure along polymer chain. The electron flow in the polymer chain is possible thanks to this conjugation structure. They are known as conducting polymers (CPs) due to their conducting features. Polypyrrole (PPy), polyaniline (PANI), Poly(3, 4- ethylenedioxythiophene) (PEDOT), and Polythiophene (PTh) are CPs studied intensely. Due to having low band gap and low redox potential these polymers show high conductivity (Cysewska *et.al.* 2015 & Groenendaal *et.al.* 2000). While PEDOT has good chemical stability (Kulandaivalu *et.al.* 2015; Patil *et.al.* 2016 & Patil *et.al.* 2016), PANI has good environmental, and thermal stability (250°C) (Kawashima & Goto 2011; Ma *et.al.* 2016) and PPy shows good redox reversibility (Li *et.al.* 2007) & Jeong *et.al.* 1998).

The polymerization of the thiophene ring simplifies when a ethylenedioxythiophene group substitutes at the 2-position of the thiophene ring, due to decreasing electron density in the ring. So, formed the linear chains are more stable than the thiophene analogous. Also, the oxidation potential of EDOT monomer is shifted at lower values because of chain is more stable. This stability is provided via the presence of the substituent containing electron-donating oxygen. the oxidation potential of (Ahmed *et.al.* 2012 & Ahonen *et.al.* 2000).

Emeraldine is the conducting form of PANI. This form composed of benzenoid or quinoid rings is one of the different oxidation form of PANI (Dhawan *et.al.* 1997; Jaymand 2013 & Bhadra *et. al.* 2009).

PPy is made of from repeating unit of pyrrole ring. This formation provides to PPy extended π -conjugated backbone along chain (Wei *et. al.* 1991 & Saville 2005).

Electrochemical Impedance Spectroscopy (EIS) is an experimental method for characterizing electrochemical systems. This method measures the impedance of the electrochemical coated carbon fiber (CF) over a range of frequencies, and the frequency response of the coated CF is determined, including the energy storage and dissipation properties, capacitive properties.

An electrical double layer forms between electrolyte and coated CF surface. This layer means electrolyte/electrode interface of a coated CF and this interface plays an important role for controlling properties such as double layer capacitance of composite and interactions on the coated surface. The capacitive behavior of coated CF was affected, as electrolyte ingredients changed. Because type and ingredients of electrolyte solution determined dielectric properties of the solution. This effect was seen in our previous studies, but was not investigated in detail.

In the presented study, we were aimed to investigate the electrical, capacitive and morphological features of the CF coated with different conducting polymers (PEDOT, PANI and PPy) and different electrolyte type (boric acid, BA, sulphuric acid, H₂SO₄ and sodium per chloride, NaClO₄, epoxy) and different solvent type (acetonitrile, ACN and /or Pure water, H₂O), comparatively. As result, we found that these parameters were affected both capacitive and electrochemical properties of coated CF and that a proportional relationship was between the morphological and the capacitive features.

2. Experimental:

Aniline (An), 3,4-Ethylenedioxythiophene (EDOT) and Pyrrole (Py) were selected as monomer. Each monomer was prepared as 0.01 M. Boric acid (BA), sulphuric acid (H₂SO₄) and sodium perchlorate (NaClO₄) as electrolyte; pure water (H₂O) or acetonitrile (ACN) as solvent were used. The electrolyte solution used in experimental tests was prepared and used as 5 ml 0.1 M. Electropolymerization tests were carried out by two different electropolymerization methods, Constant Potential Electropolymerization (CPE) and Cyclic Voltammetry (CV) in three electrode system. In this system Ag wire was used as reference electrode (calibrated with 0,1 M ferrocene), Pt wire as counter electrode and Carbon Fiber (CF) as working electrode. Working electrode was prepared in brush form (0.003+- 0.0005 g and 6cm) for CPE tests and in single fiber form for CV tests. Epoxy based compound (EBC, Chemetylen AK-2) was provided from SANYO Chemical Industries, Ltd.

3.Results and discussion:

3.1. The Constant Potential Electropolymerization (CPE):

To investigate the effect of different polymer on electrical behavior of CF, the CFs in form of brush were electrocoated with different polymers (PAn, PEDOT and PPy) at constant potential (1V) produced by a power supply in the same electrolyte medium. In this part EBC was not added in the electrolyte media. Obtained data were plotted in Figure 1.

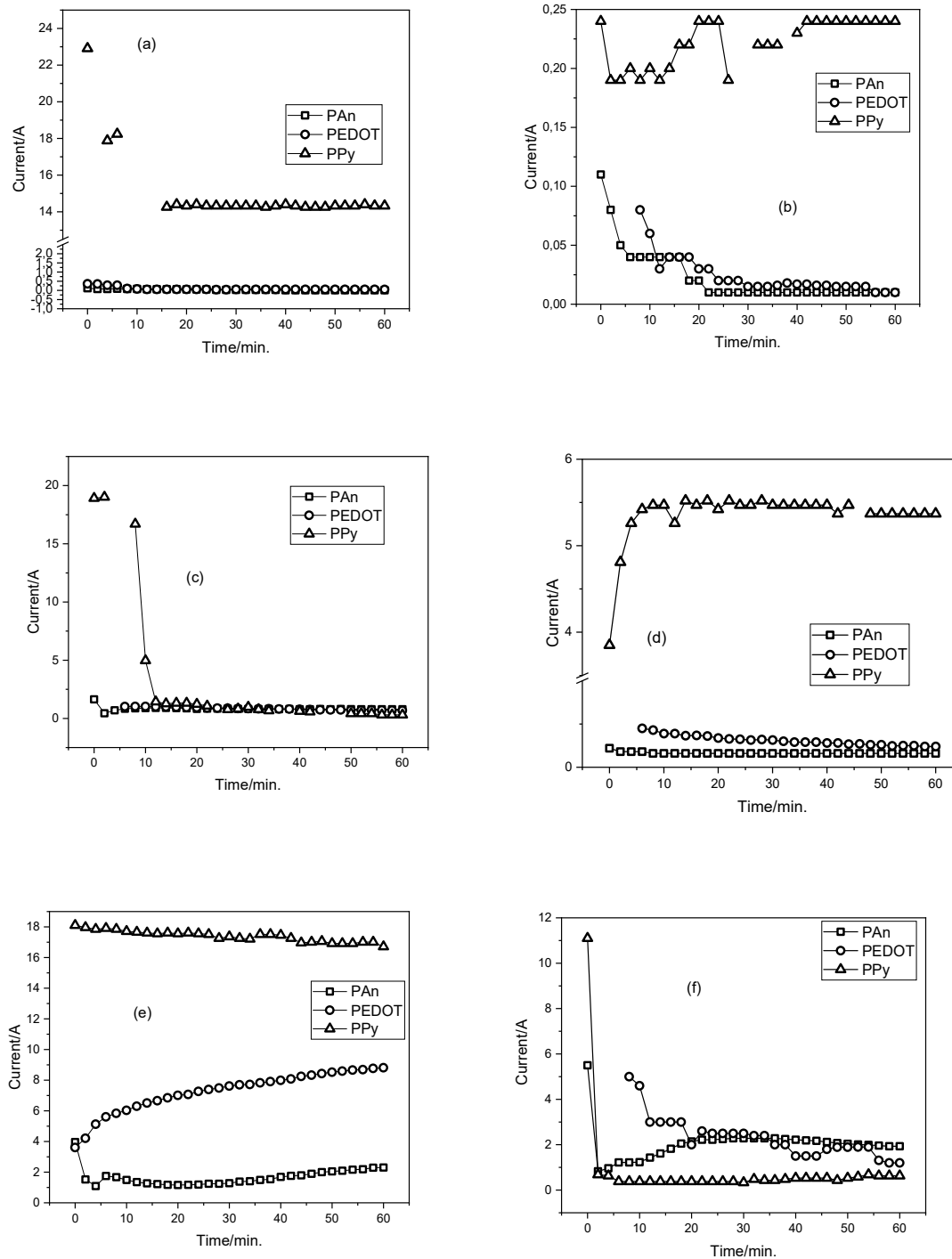


Figure 1. The Current-Time graph. a) BA-H₂O-0% EBC; b) BA-H₂O- 1.8% EBC; c) H₂SO₄-H₂O-0% EBC; d) H₂SO₄-H₂O-1,8% EBC; e) NaClO₄-ACN- 0% EBC; f) NaClO₄-ACN- 1.8% EBC. (monomer concentration: 0.1M)

The species in electrolyte solution such as solvent, monomer or other material affected electron movement in

solution due to ionic strength and/or action with each other. For this reason, formed current in solution was increased or decreased. As seen from figure 1c current data passed system was reached to about range of 6-7 A for PEDOT sample, 1-1.5A for Pan and 17-18 A for PPy in NaClO₄-ACN, compared with the other solution media. Current flown in system was decreased in BA-H₂O and H₂SO₄-H₂O medium due to the interaction of monomer and electrolyte.

To see the effect of different a material in electrolyte solution, given above experimental conditions were repeated by adding the EBC in electrolyte solution as %1.8 (w/w). Obtained data were plotted in Figure 1b, d, and f, comparatively with 0% EBC.

It was seen that the current flown in system was decreased/increased in certain values for each monomer. But this changing was more for Py than that for the other. When it was not remarkably for An and EDOT monomers from the Fig, with compared to Py. So, the current value was changed to 0.24 from 14.33 A in BA-H₂O, to 5.37 from 0.31 A in H₂SO₄-H₂O, to 0.63 from 16.71 A in NaClO₄-ACN for Py; to 0.01 from 0.05 A in BA-H₂O, to 0.24 from 0.69 A in H₂SO₄-H₂O, to 1.2 from 8.81 A in NaClO₄-ACN for EDOT; to 0.01 from 0.01 in BA-H₂O, to 0.16 from 0.79 A in H₂SO₄-H₂O, to 1.93 from 2.3 A in NaClO₄-ACN for An. This case could be attributed the interaction of between monomer or electrolyte and EBC.

Obtained coated CFs with conducting polymer in different experimental conditions were weighed at analytical balance to investigate the relation of condition-coating weight. The coated CF was dried in air and weighed. The weight of uncoated CF was subtracted from this value. Obtained data were given in Figure 2.

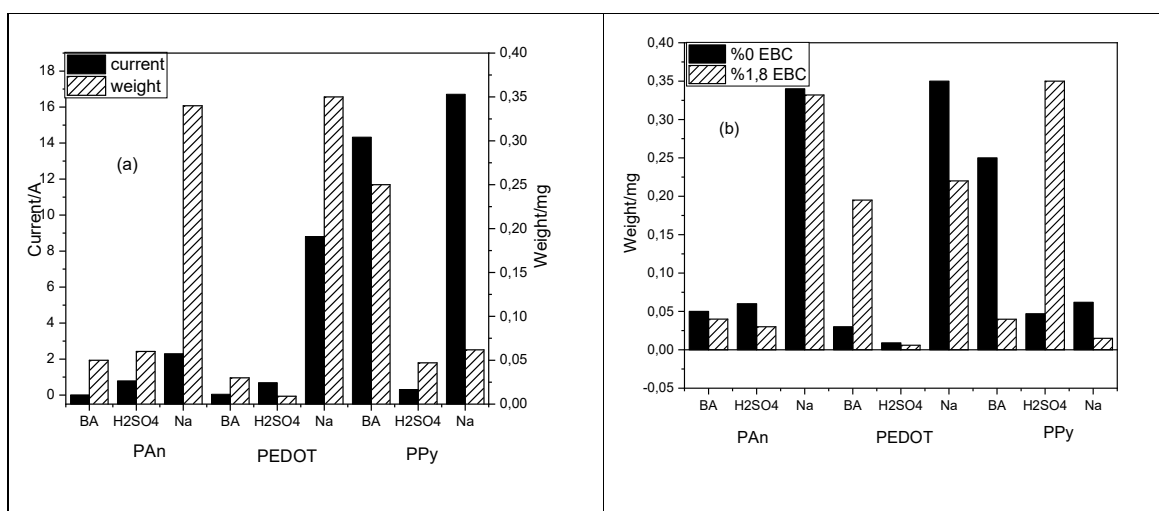


Figure 2. The graph of the Current passed in system –the Weight of coating by CPE method. a) 0% EBC; b) comparison.

It was seen that the weight of coating was increased for PAN sample in different electrolyte medium as current was increased. This changing was observed as decreasing in presence of %1.8 EBC (Figure 2b). So, the weight of coating was decreased in different electrolyte medium in presence of %1.8 EBC, in parallel with the current. For PEDOT and PPy this manner was different. The weight was increased in presence of EBC in BA for PEDOT, in H₂SO₄ for PPy even though the current was decreased. This case might be excess of H⁺ ions in electrolyte medium.

It was thought that the impedance value of the coated CF with conducting polymer was affected by electrocoating conditions. For this reason, the coated CFs obtained in various conditions were electro performed in monomer free electrolyte solution at different scan rates. To evaluate the impedance of the CFs, the double layer capacitance (C_{DL}) and the Phase Angle of coated CF were plotted Figure 3, comparatively.

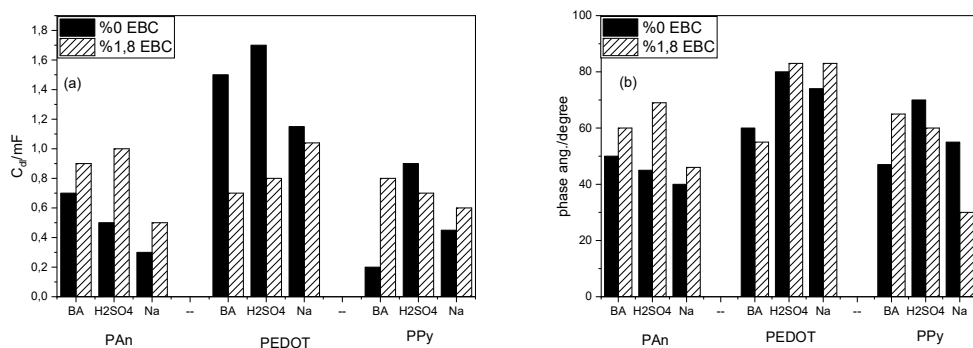


Figure 3. The Impedance graphs of CF coated with different conditions by CPE method. a) The C_{DL} graph, b) The Phase Angle graph.

When it was looked at the Figure 3 it can be seen that C_{DL} and Phase Angle were parallel together. The experiments were carried out in cyclic voltammetry (CV) because of that to investigate the electrical and capacitive manner of CFs coated with different conducting polymer by controlled potential method. The applied conditions and used parameters of electrocoating were same the in CPE method, except for CF brush form. The single CFs were used for CV experiments. Read maximum current and the oxidation potential of each monomer (An, EDOT, Py) values were plotted in Figure 4 compared with 1.8 % EBC.

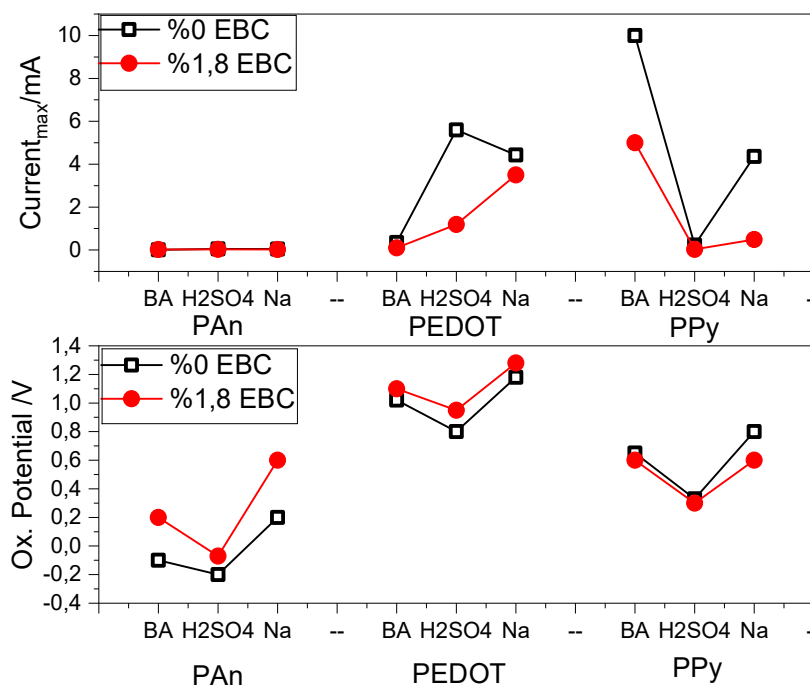


Figure 4. The comparison graphs of (a) The maximum current and (b) The oxidation potential belonging to PAn, PEDOT and PPy coatings obtained in different electrocoating conditions.

According to data, the oxidation was observed at lower potential in H_2SO_4 electrolyte solution for all monomers compared with other solutions. Beside this, in presence of EBC the potential was increased for PAn and PEDOT when it was decreased for Py. I_{max} values were changed for each polymer and conditions. Lowest value was read as $0.35 \cdot 10^{-5}$ A for PEDOT in BA and $0.23 \cdot 10^{-5}$ A for PPy in H_2SO_4 . In presence of EBC the value was not changed importantly but, it was decreased for PEDOT and PPy and electrolytes. The biggest decreasing was $4.5 \cdot 10^{-5}$ A in H_2SO_4 for PEDOT and $5 \cdot 10^{-5}$ A in BA for PPy.

The CFs coated with different electropolymerization conditions such as monomer, electrolyte, solvent and adding EBC by CV method were scanned in monomer free solution at different rates and at electrocoating potential range to investigate the capacitive and electrical properties of the CFs. Addition obtained this data supplied the information about if the electropolymerization mechanism was controlled by diffusion in absence/presence of EBC. In this section it was taken advantage of Randles-Sevcik equation.

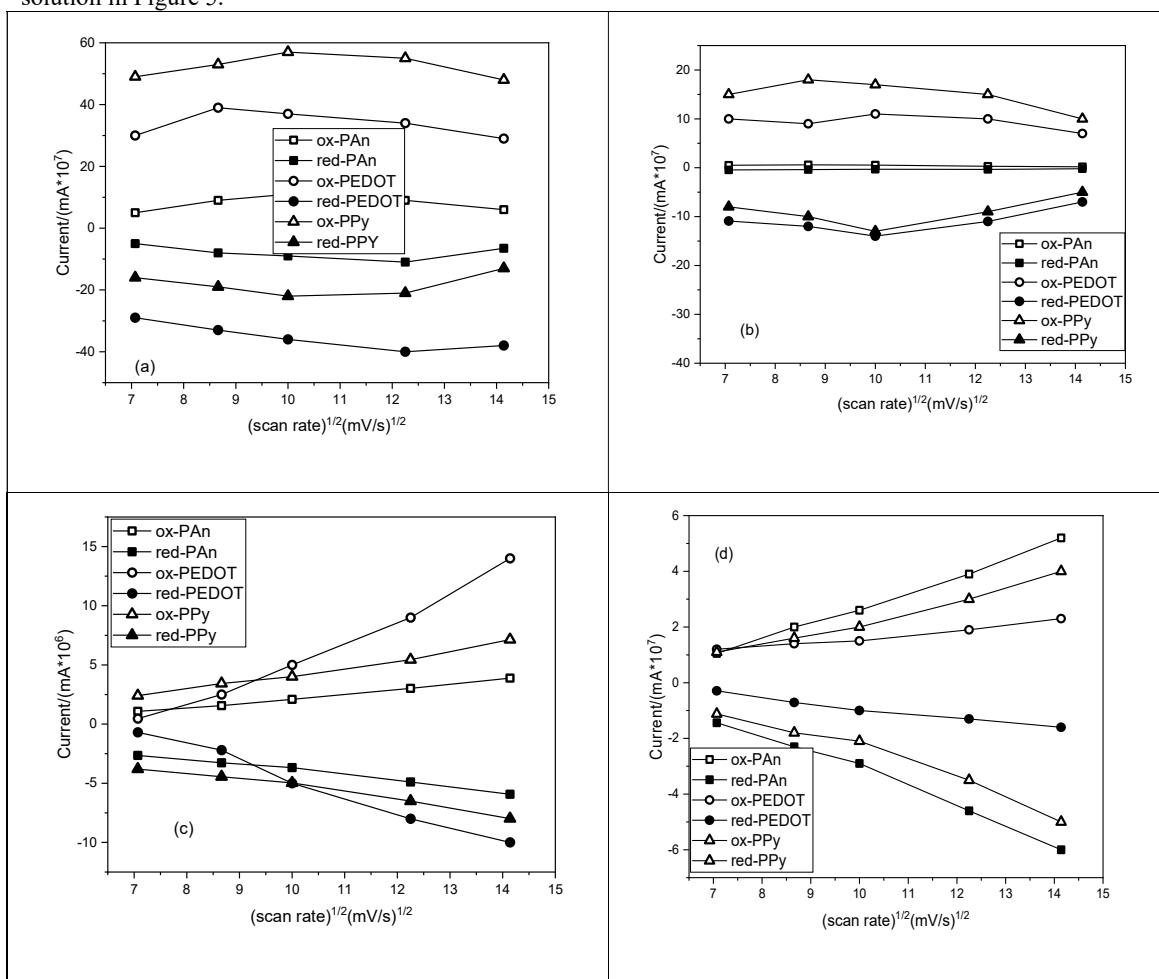
In electrochemistry, this equation describes the effect of scan rate on the peak current of the oxidation and reduction (I_p).

$$I_p = 0,4463nFAC\sqrt{\left(\frac{nFvD}{RT}\right)} \quad (1)$$

Or, if the solution is at 25°C,

$$I_p = 2,65 * 10^5 ACn^{3/2}(Dv)^{1/2} \quad (2)$$

In electrocoated process, the current passing through the electrode coated with conducting polymer is limited by the diffusion of species to the electrode surface from electrolyte solution medium. This diffusion flux is affected by the ingredients of electrolyte solution and the species at the electrode. As the plots of I_p vs. $v^{1/2}$ was linear, it can say that the redox process was a chemically reversible process. So, obtained the oxidation ($I_{p,ox}$) and reduction ($I_{p,red}$) current peak values in different scan rates were illustrated for each monomer and electrolyte solution in Figure 5.



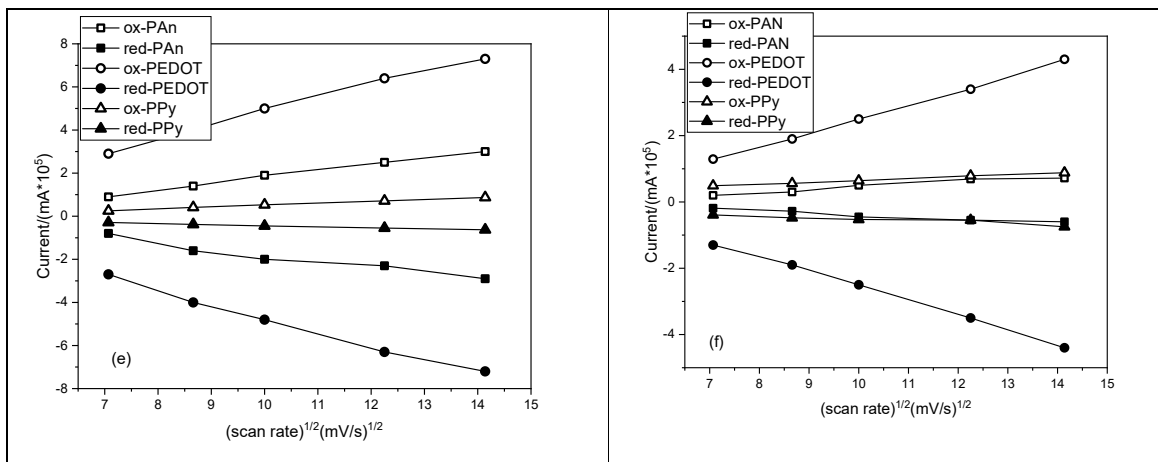


Figure 5. The graphs of the ox. and red. peak current vs. the square root of scan rate. a) BA-H₂O-0% EBC; b) BA-H₂O-1.8% EBC; c) H₂SO₄-H₂O-0% EBC; d) H₂SO₄-H₂O-1.8% EBC; e) NaClO₄-ACN- 0% EBC; f) NaClO₄-ACN- 1.8% EBC.

According to Randles-Sevcik equation, obtained plots in BA-H₂O were not linear for all polymers (Figure 5a, c, e). In this case, it can be said that the redox process was not controlled by diffusion under this conditions. On the other hand, it was seen that all the redox processes carried out in NaClO₄-ACN electrolyte solution were controlled by diffusion for each polymer coated CFs due to linear plot. In this conditions diffusion coefficient (D) was bigger than that of the Pan and PPy for PEDOT, because of high I_p value.

To investigate whether the redox process was controlled by diffusion or not in presence of %1.8 EBC in electrolyte solution, scanning at different rates were performed in the same conditions but adding %1.8 EBC. Taken data were plotted in Figure 5b, d, e for BA-H₂O, H₂SO₄-H₂O and NaClO₄-ACN, respectively. In presence of EBC it could be say that redox process was controlled by diffusion in BA-H₂O for PAN in comparison with others. But D was low due to I_p value. The process was proceeded by controlling with diffusion in NaClO₄-ACN for PEDOT but not for Pan and PPy. This result was seen in previous study for PPy in same medium (Dolas et.al. 2016).

According to the determined results, it could be concluded that redox process mechanism was controlled or not by diffusion as depending on the used polymer and the species in electrolyte solution. This case might be attributed to the interaction of polymer and the species in electrolyte.

The C_{DL} and phase degree of the CFs coated with PAN, PEDOT or PPy in the above mentioned electrolyte conditions were given in Figure 6.

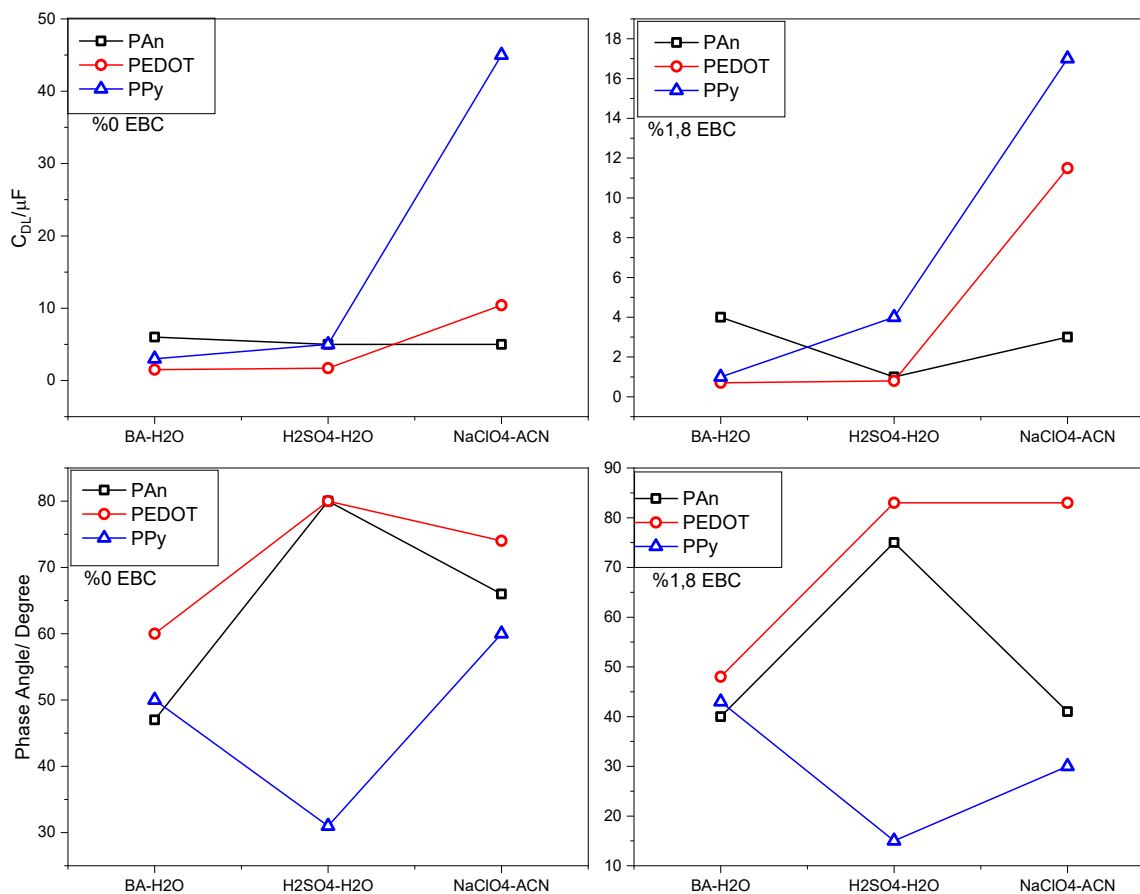


Figure 6. The Impedance graphs of CF coated with different conditions by CV method. a) The C_{DL} graph, b) The Phase Angle graph.

The plots written 1.8 % EBC in the figure expressed the presence of 1.8 % EBC in electrolyte solution. When it was comparatively looked at the plots it was seen that the C_{DL} value was decreased in every electrolyte solution for each one polymer in presence of 1.8 % EBC in electrolyte solution. So, this value was decreased to 4 μF from 6 μF ; to 0.7 μF from 1.5 μF ; to 1 μF from 3 μF in BA-H₂O for Pan, PEDOT and PPy respectively. This decreasing trend was seen in the other conditions for the polymers. But, C_{DL} was increased to 11.5 μF from 10.4 μF in NaClO₄-ACN for PEDOT. Phase angle was in the same trend. The feature was increased to 83 ° from 74 ° in NaClO₄-ACN for PEDOT while it was decreased in all electrolyte solutions for Pan and PPy in presence of EBC.

The electropolymerization of conducting polymers were started by applied a potential at a certain of voltage. The electron motion was supplied due to the resonance structure of monomer ring. Thus, formed polymer chain was closed to electrode (here CF) and CF was coated with conducting polymer. This formation was represented as the coating of CF with PEDOT in Figure 7.

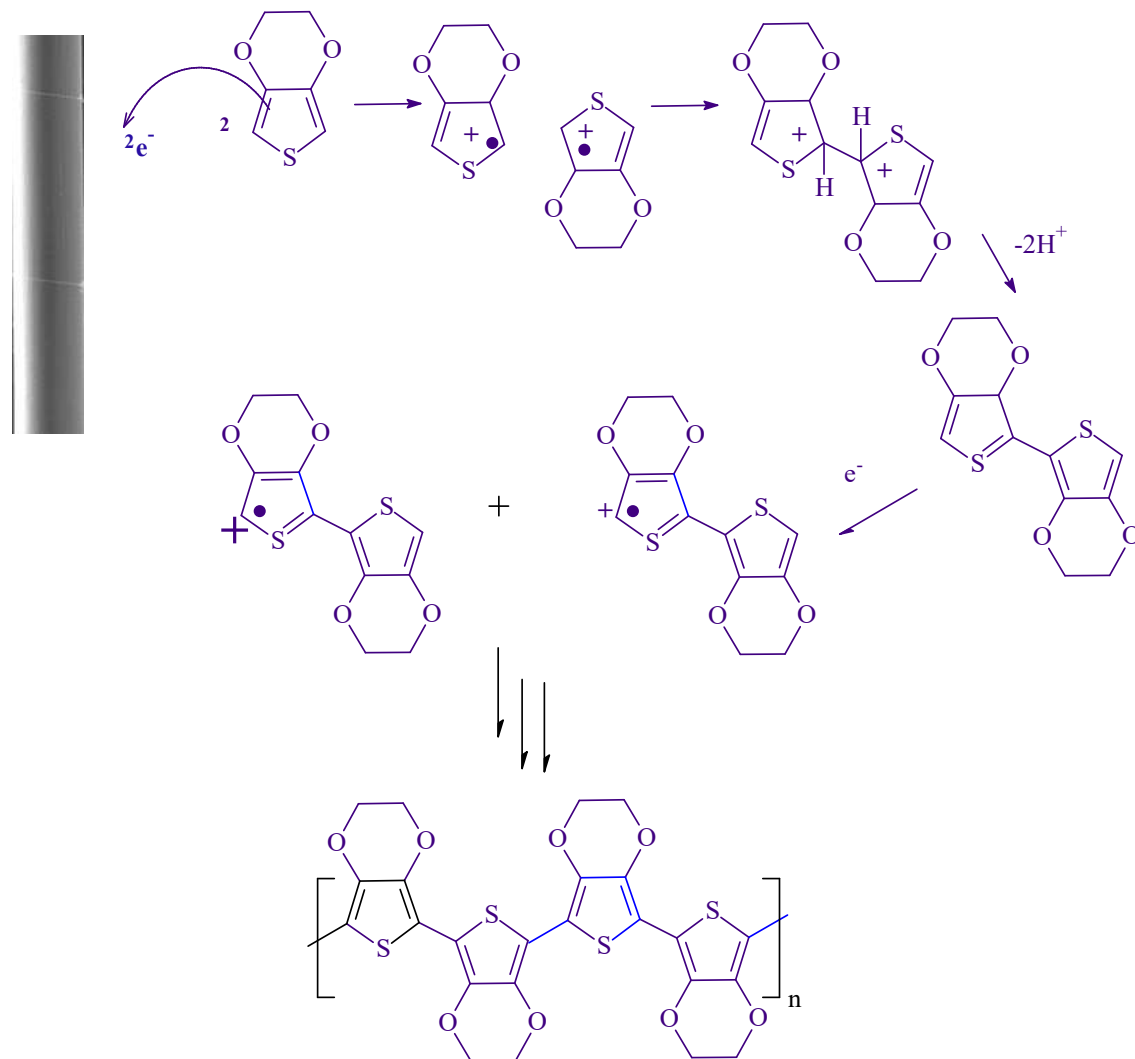


Figure 7. The presentation of the coating CF with PEDOT by CV method in electrolyte solution.

The motion of electron and monomer were affected by the structure and type of species in solution. So, the morphological differences were formed by this effects. For this reason, to show these differences, the SEM images of coated CFs were given in Figure 8. Figure 8b and 8d presented the SEM image of 5 mM PEDOT and 5mM PPy coated CF in presence of EBC in $NaClO_4/CAN$, respectively.

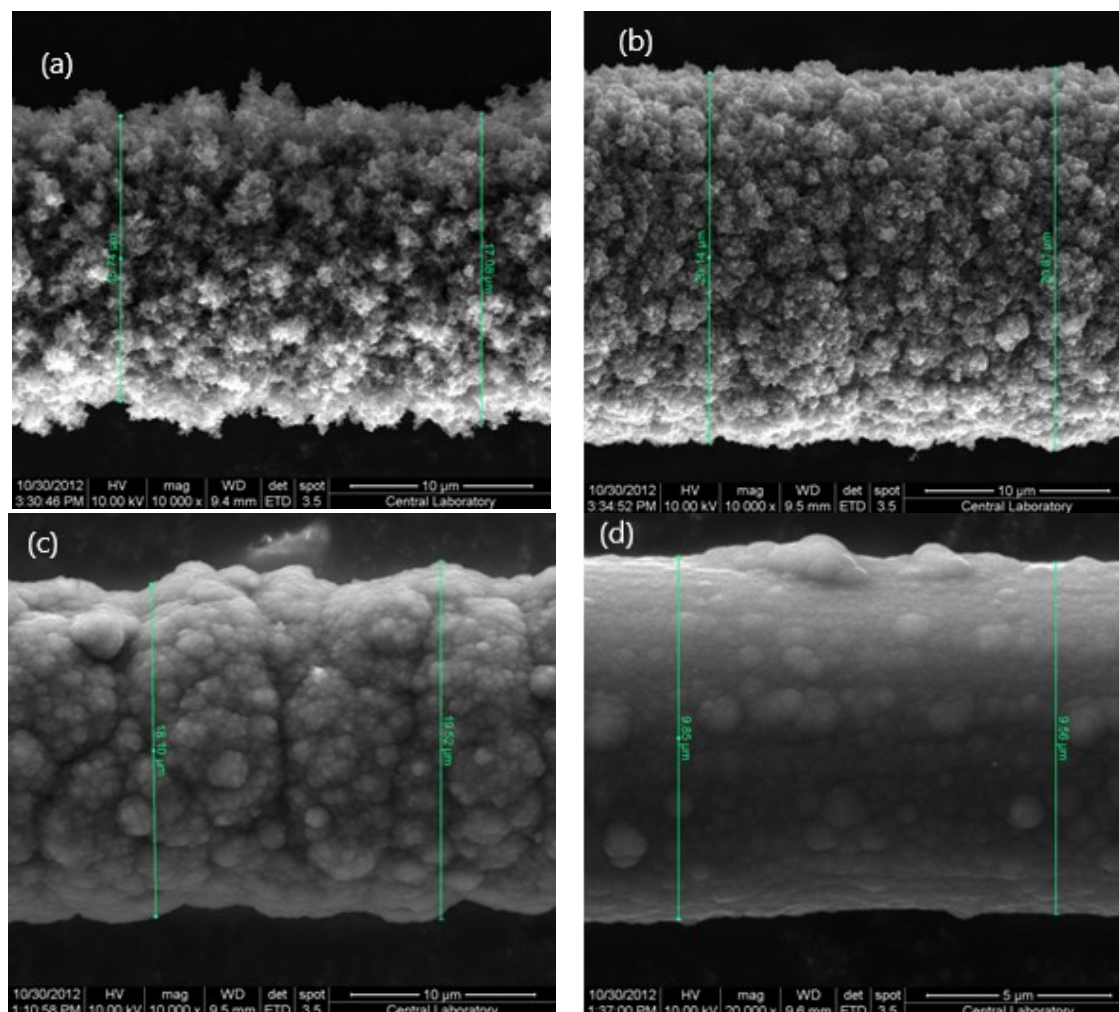


Figure 8. The SEM images the CF coated with a) PEDOT in NaClO₄-ACN, b) PEDOT in NaClO₄-ACN-%1.8 EBC, c) PPy in NaClO₄-ACN, b) PPy in NaClO₄-ACN-%1.8 EBC.

It can be seen that the texture coatings were more compact in the presence of EBC in electrolyte solution than that of the absence of EBC for PPy coated CF. The radius of PPy coated CF was measured as 9.85 μm in % 1.8 EBC (Figure 8d), while it was measured as 18.10 in %0 EBC. On the contrary, according to taken SEM images the texture coating were more compact in the absence of EBC in electrolyte solution. The radius of PEDOT coated CF was measured as 17.05 for %0 EBC, while it was measured as 20.14 for %1.8 EBC. This manner can be attributed to the interaction and/or tendency in between the monomer and EBC due to their chemical structures.

Obtained C_{DL} and radius data were compared to determine the relationship of between the radius of coating and the C_{DL} of the coated CF. Thus, the data were given Table 1.

Table 1: The relationship of between the radius of coating and the C_{DL} of the coated CF

Conditions	PEDOT		PPy	
	C _{DL} / μF	Radius / μm	C _{DL} / μF	Radius / μm
0% EBC	10.4	17.05	45	18.10
1,8 % EBC	11.5	20.14	17	9.85

As according to the data in Table 1, it was seen that the relationship of between the radius of coating and the CDL of the coated CF was proportional. The relationship was proved that as radius was increased, capacitance value was increased as it was in PEDOT sample and as radius was decreased, capacitance value was decreased as it was in PPy sample.

4. Conclusion:

In this study, it was investigated CFs were coated electrochemically with three different monomers (An, EDOT or Py) in different condition such as electrolyte (BA, H₂SO₄ or NaClO₄), solvent (H₂O as inorganic medium or ACN as organic medium), in presence of foreign material (EBC) and coating method (constant potential and cyclic voltammetry as controlled potential). Obtained CFs coated with conducting polymer different conditions were compared with regard to electrical and capacitive and morphological features. These features were the current passed in the system, the weight of coating, C_{DL}, phase angle, ox. and red. Peak current, diffusion controlling, the radius of coating, the texture of coating.

It was determined that in CPE, the current passed in the system was reached to about range of 6-7 A for PEDOT sample, 1-1.5A for Pan and 17-18 A for PPy. Thus the current was decreased in BA-H₂O and H₂SO₄-H₂O medium due to the interaction of monomer and electrolyte. It was seen that the current flow in system was changed in certain values for each monomer by adding the EBC in electrolyte solution as %1.8 (w/w). But this changing was more for Py than that for the other. When it was not remarkably for An and EDOT monomers, with compared to Py. This case was concluded that the case was based on the interaction of between monomer or electrolyte and EBC.

According to data, the oxidation was observed at lower potential in H₂SO₄ electrolyte solution for all monomers compared with other solutions. Beside this, in presence of EBC the potential was increased for PAN and PEDOT when it was decreased for Py. I_{max} values were changed for each polymer and conditions.

According to Randles-Sevcik equation, obtained plots in BA-H₂O were not linear for all polymers. In this case, it could be concluded that the redox process was not controlled by diffusion under this conditions. On the other hand, it was seen that all the redox processes carried out in NaClO₄-ACN electrolyte solution were controlled by diffusion for each polymer coated CFs due to linear plot. In this conditions diffusion coefficient (D) was bigger than that of the Pan and PPy for PEDOT, because of high I_p value.

In presence of EBC it could be concluded that redox process was controlled by diffusion in BA-H₂O for PAN in comparison with others. But D was low due to I_p value. The process was proceeded by controlling with diffusion in NaClO₄-ACN for PEDOT but not for Pan and PPy.

As seen that the related plots, the C_{DL} value was decreased in every electrolyte solution for each one polymer in presence of 1,8 % EBC in electrolyte solution. So, this value was decreased to 4 μF from 6 μF; to 0.7 μF from 1.5 μF; to 1 μF from 3 μF in BA-H₂O for Pan, PEDOT and PPy respectively. This decreasing trend was seen in the other conditions for the polymers. But, C_{DL} was increased to 11.5 μF from 10.4 μF in NaClO₄-ACN for PEDOT. Phase angle was in the same trend. The feature was increased to 83 ° from 74° in NaClO₄-ACN for PEDOT while it was decreased in all electrolyte solutions for Pan and PPy in presence of EBC.

The texture coatings were more compact in the presence of EBC in electrolyte solution than that of the absence of EBC for PPy coated CF. When obtained C_{DL} and radius values from different from conditions were compared it was seen that the relationship of between the radius of coating and the C_{DL} of the coated CF was proportional. Thus, it may be concluded that the C_{DL} and radius of coating were affected with the presence of different material/compound in electrolyte solution.

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