

CORROSION OF STEEL IN IONIC LIQUIDS

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Abstract

The corrosion behavior of 1018 carbon steel alloy has been investigated by electrochemical techniques. The ionic liquids studied were 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim]PF_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim]PF_6$), and 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imide ($[C_4mim][Tf_2N]$). Potentiodynamic polarization and Tafel plots were used to determine the corrosion behavior of the carbon steel. Results showed that corrosion resistance of 1018 carbon steel in ionic liquids is outstanding as indicated by the low corrosion rates obtained which ranged from 3-13 $\mu m/yr$. Anodic polarization curves showed active/passive corrosion behavior of the alloy in most of the ionic liquids tested. However, ionic liquids containing chloride ions were unable to form a passive region.

Keywords: corrosion, corrosion potential, ionic liquids, carbon steel

1. Introduction

Solar energy technology is capable to produce clean, cost-effective, dispatchable electric power on a very large scale, without harmful pollutants or carbon emissions. Solar thermal power plants based on parabolic trough collectors are presently the most successful solar technology for electricity generation [1-3]. The solar receiver consists of a large array of parabolic collectors that reflect the sunlight to a black absorber steel tube that lies in the focus line. The concentrated solar energy is transferred to a fluid,

which is heated as it circulates through the receiver. The hot fluid flows through a series of heat exchangers, thus generating high-pressure superheated steam. In the majority of operations, oil-based fluids are used as heat transfer media [4]. However, future plants will require the utilization of heat transfer fluids with improved properties. Due to their unique combination of properties, such as low vapor pressure and high heat capacity, ionic liquids have been proposed as both heat transfer and storage liquids [5].

Ionic liquids are liquids that are entirely comprised of ions. Their structure is usually composed of an organic cation and inorganic anion. Ionic liquids of interest are based on the imidazolium cation (1-alkyl-3-methylimidazolium), whose structure is shown in Fig.1 [6]. Common anions are $[PF_6]^-$, $[Cl]^-$, $[BF_4]^-$, and $[Tf_2N]^-$. It is only in recent years that significant literature on the properties of ionic liquids has become available [7-9]. However, reports on the corrosivity of ionic liquids against engineering alloys have not been found in the technical literature. This property is of importance in parabolic trough plants where corrosion of steel pipes needs to be avoided.

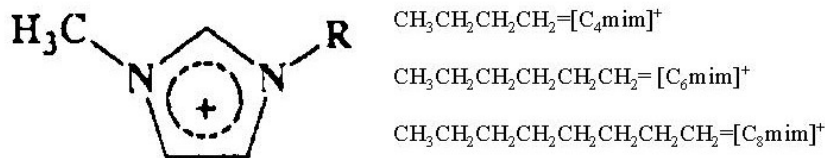


Figure 1. Structure of imidazolium cation (1-alkyl-3-methylimidazolium).

In this study, the corrosion behavior of 1018 carbon steel in selected imidazolium based ionic liquids was studied using electrochemical techniques. The principal objective was to assess the relationship between the corrosion rate at room temperature and the structure of the ionic liquid. Data from this study is considered to be essential for developing an understanding of the role of the structure of ionic liquids in modifying the corrosion behavior of the alloy. Among the electrochemical techniques, potentiodynamic polarization was selected since it has been used extensively to characterize corrosion of metal alloys in specific environments.

2. Experimental

2.1. Synthesis of ionic liquids

Four ionic liquids were tested: 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$),

1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim]PF_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim]PF_6$), and 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imide ($[C_4mim][Tf_2N]$). These ionic liquids were synthesized according to the procedure described in earlier publication [6]. Synthesis via exchange reactions was applied for all ionic liquids. After the reaction, the product and unreacted initial chemicals were separated into two liquid layers. The top layer consisting of impurities was decanted, while the remaining product was washed with ethyl acetate for several times. Vacuum was applied for removing unreacted chemicals and washing liquids.

2.2. Corrosion tests

A Pyrex glass cell with a capacity of 300 ml was used for the electrochemical corrosion tests. The system was composed of a typical three-electrode arrangement consisting of a working electrode, auxiliary electrode, and reference electrode. The auxiliary electrode was made of platinum foil spot-welded to a platinum wire that was sealed into Pyrex. An Accumet™ saturated calomel reference electrode was placed in a 30-ml separatory funnel outside the cell. A Luggin probe-salt bridge, with a closed solution-wet stopcock to eliminate leakage, separated the ionic liquid solution from the saturated calomel reference electrode. The probe tip was easily adjusted to bring it at a distance of about 2mm from the working electrode. A potentiostat (Model 273A by EG&G Princeton Applied Research) was used for the electrochemical measurements. Model 352/252 corrosion analysis software (EG&G ver. 2.01) was used to analyze the data and calculate the Tafel constants.

The 1018 carbon steel alloy was obtained from McMaster-Carr Supply Company in the form of plates and its composition is shown in Table 1. The specimens were cut and mounted in epoxy resin leaving a carefully measured surface area of 10x10 mm for exposure. Before mounting, electrical contact was made to each specimen using silver paste to attach a copper wire to the back surface of specimen. The surface was ground with 240-grit SiC paper, and then polished sequentially on 240, 320, 400, and 600 grit SiC paper until previous coarse scratches were removed. Just prior to immersion, the specimen was degreased with acetone, rinsed in distilled water, and then dried. Most of the tests were conducted in air, except for the moisture sensitive ionic liquid $[C_4mim]Cl$, which was tested in a glove box under argon gas atmosphere. Two techniques, namely Tafel plots and polarization curves were used to study the corrosion behavior of the alloys in ionic liquids. The first technique allowed the determination of corrosion potential E_{corr} and corrosion current I_{corr} . Corrosion current I_{corr} was determined by the Tafel extrapolation method by carrying out scans in both the positive and negative directions with respect to the corrosion potential of 250 mV each. As a result, a polarization curve consisting of both anodic and cathodic segments was obtained. Based on

Table 1. Composition of the alloy tested in the corrosion experiments

Alloy	Chemical composition (wt %)			
	C	Mn	P	S
1018 steel	0.14-0.20	0.60-0.90	0.035	0.040

I_{corr} values, the corrosion rate of the alloy in ionic liquids was calculated. The potentiodynamic polarization curves of all the specimens were generated after conducting the scan from -250 mV below E_{corr} to $+1.6$ V (versus saturated calomel electrode) at a sweep rate of 10 mV/min. The potentiodynamic plots were produced directly using the data acquisition system. All tests were performed at room temperature.

3. Results and Discussion

3.1. Determination of corrosion rates

Tafel plots obtained in this study are shown in Figures 2-5. Extrapolation of the applied current density from either cathodic or anodic Tafel region to the open-circuit potential in a plot of potential vs. $\log I_0$, gives the corrosion current density I_{corr} . Corrosion rate for uniform corrosion can be expressed by the following equation [10]:

$$r = \frac{3.27 \times 10^{-3} \cdot i_{corr} \cdot W}{\rho} \quad (1)$$

where r is corrosion rate in millimeters per year, W is equivalent weight in grams, ρ is the density of the metal or alloy in g/cm^3 , and i_{corr} is corrosion current density in $\mu\text{A/cm}^2$.

For alloys, the equivalent weight W can be calculated using the atomic mass fractions of each alloying element in an expression such as:

$$W = \frac{I}{\sum_{i=1}^m \frac{x_i z_i}{M_i}} \quad (2)$$

where x_i , z_i and M_i are atomic mass fraction, electron exchanged, and atomic weight respectively.

The equivalent weight for carbon steel is 27.92 and the density is 7.87 g/cm^3 . Therefore, based on the corrosion current densities determined in the present study, the uniform corrosion rates of 1018 carbon steel in ionic liquids can be calculated by Eq.(1). The results of calculation are tabulated in Table 2. As can be seen in this table, corrosion rates range from 3 - 13 $\mu\text{m/yr}$. Materials with a corrosion rate less than 0.02 mm/yr are

generally considered outstanding in relative corrosion resistance [10]. Therefore, the alloys tested in this research are considered outstanding in corrosion resistance to the ionic liquids studied here. The possibility of localized corrosion was studied by potentiodynamic testing.

Table 2. Corrosion rates of 1018 carbon steel in different ionic liquids

Ionic Liquid	1018 Carbon Steel		
	Corrosion Potential V	Corrosion Current $\mu\text{A}/\text{cm}^2$	Corrosion rate, r $\mu\text{m}/\text{yr}$
$[\text{C}_4\text{mim}]\text{Cl}$	-0.298	0.27	5.6
$[\text{C}_6\text{mim}]\text{PF}_6$	-0.400	1.12	13
$[\text{C}_8\text{mim}]\text{PF}_6$	-0.247	0.47	3.2
$[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$	-0.43	0.99	11

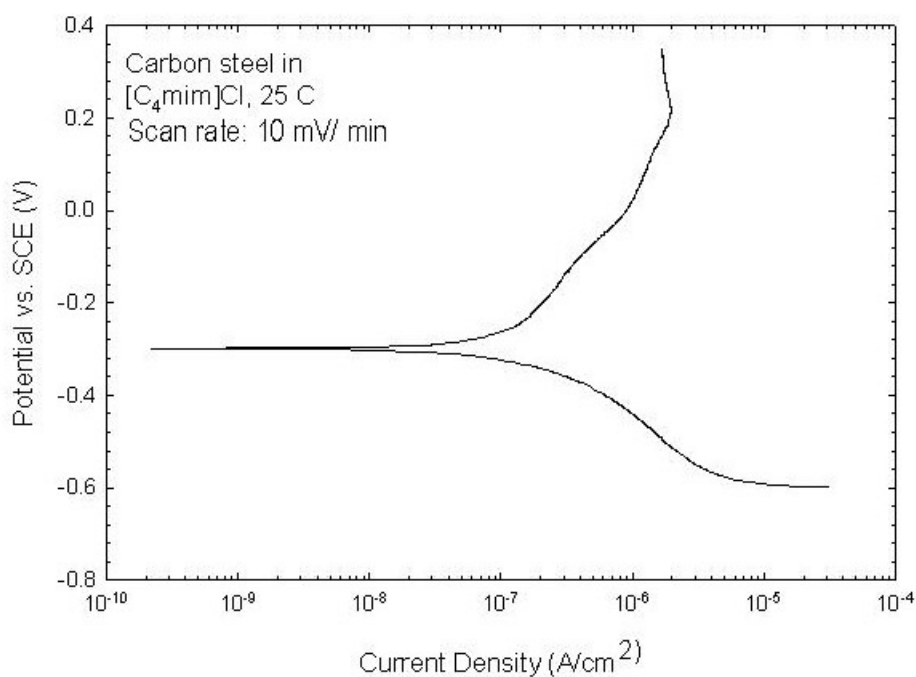


Figure 2. Tafel plot obtained for 1018 carbon steel in $[\text{C}_4\text{mim}]\text{Cl}$ at 25 °C.

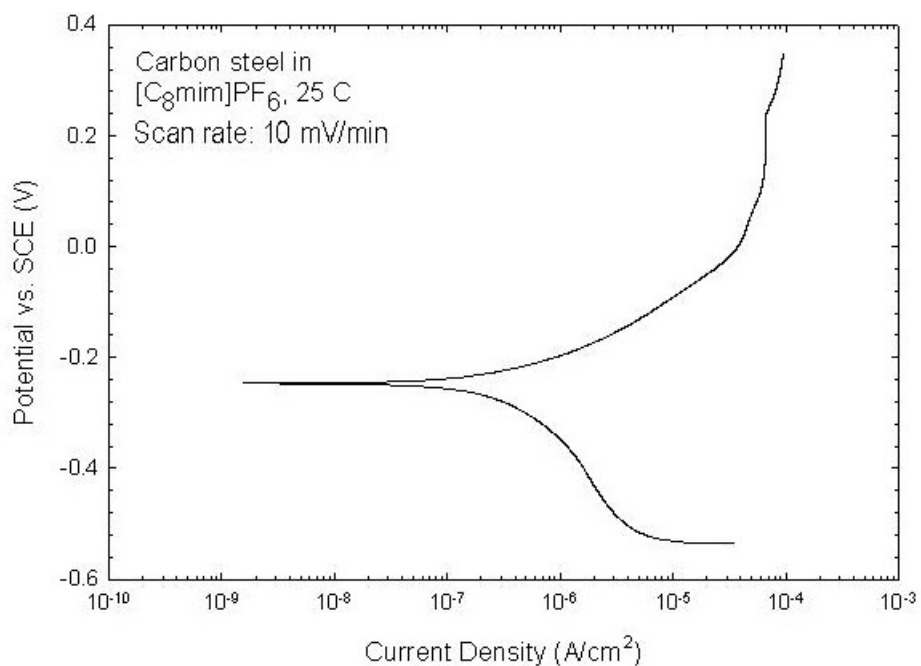


Figure 3. Tafel plot obtained for 1018 carbon steel in [C₈mim]PF₆ at 25 °C.

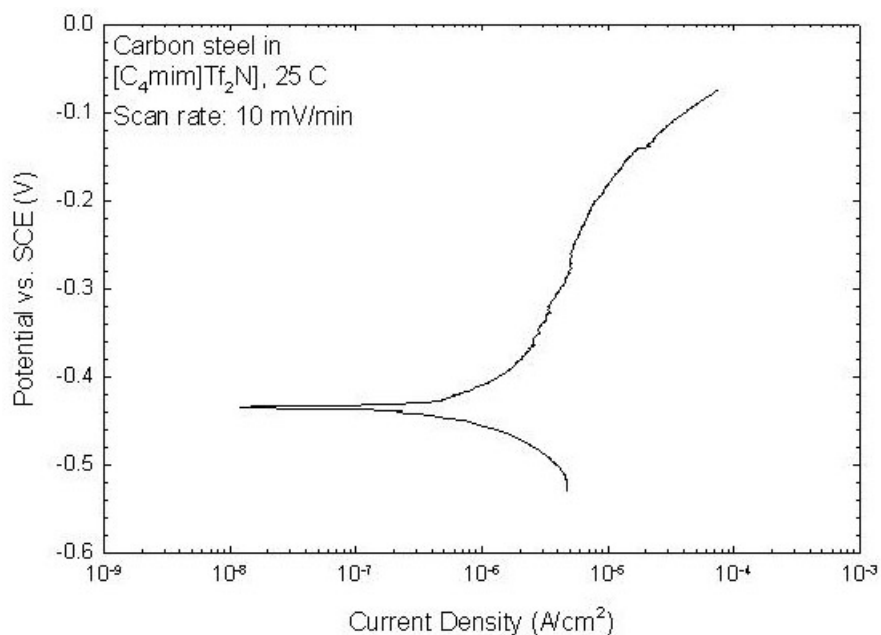


Figure 4. Tafel plot obtained for 1018 carbon steel in [C₄mim]Tf₂N at 25 °C.

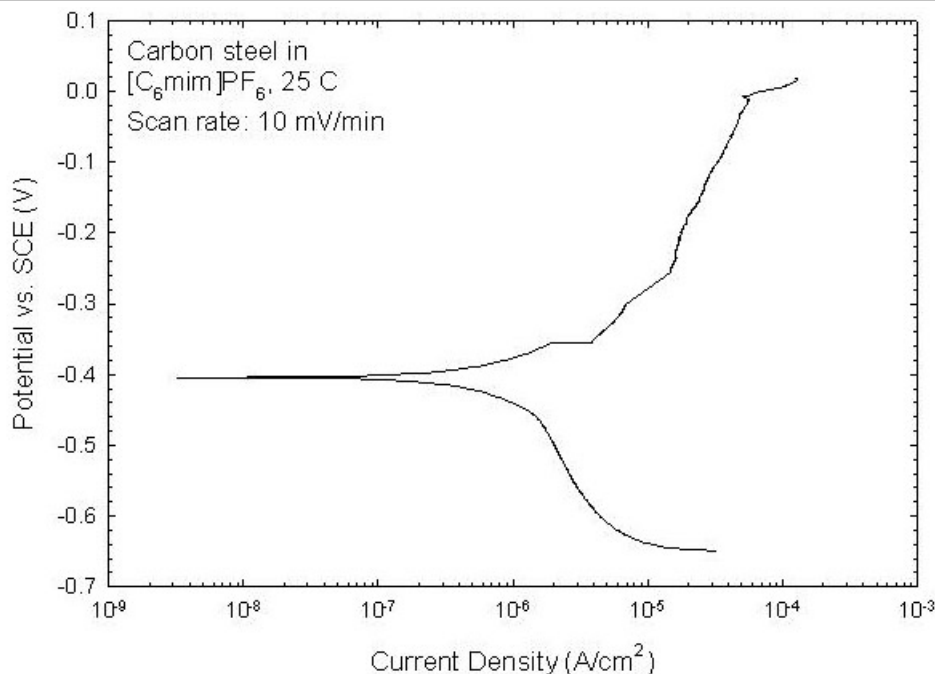


Figure 5. Tafel plot obtained for 1018 carbon steel in $[C_6mim]PF_6$ at 25 °C.

3.2. Electrochemical potentiodynamic behavior

The characteristics of potentiodynamic anodic polarization curves provided an insight into the corrosion behavior of the alloys. Figs. 6 to 9 show the polarization plots for carbon steel in various ionic liquids at 25 °C. Fig.6 shows the results for 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imide ($[C_4mim][Tf_2N]$). It can be seen that the region of active dissolution ranges from -0.45 V to 0.2 V. Higher potentials yielded a decrease of about one order of magnitude in corrosion density. Fig.7 shows the results for 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$). In this figure, corrosion takes place between -0.3 V and 0.2 V while between 0.3 and 0.7 V current density is independent of potential. At higher potential values the alloy dissolved actively indicating that in $[C_4mim]Cl$ no stable passive films are formed. The presence of chloride in the electrolyte may restrict the stability of any oxidized film, leading to localized corrosion by film breakdown. Fig.8 presents the results for 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim]PF_6$). This figure shows a region of dissolution between -0.4 V to about 0.1 V. Further potential increase up to 0.8 V resulted in weak passivation. However, at higher potentials ($>0.8V$), more pronounced passivation was observed as evidenced by the drop of about one order of magnitude in current density. Fig.9 shows the results for 1-octyl-3-methylimidazolium hexafluoro-

rophosphate ($[C_8mim]PF_6$). This figure indicates active dissolution of the alloy between -0.2 V to about 0.1 V. Further increase in voltage results in weak passivation as shown by both the small increase in current density between 0.1 and 0.8 V and the slight decrease of the same variable at higher potentials. In summary, polarization curves of 1018 carbon steel have shown active/passive corrosion behavior in most ionic liquids except for $[C_4mim]Cl$. Despite the low corrosion rates obtained in this ionic liquid, it was evident that the carbon steel alloy is prone to localized corrosion due to the presence of the deleterious Cl^- ion.

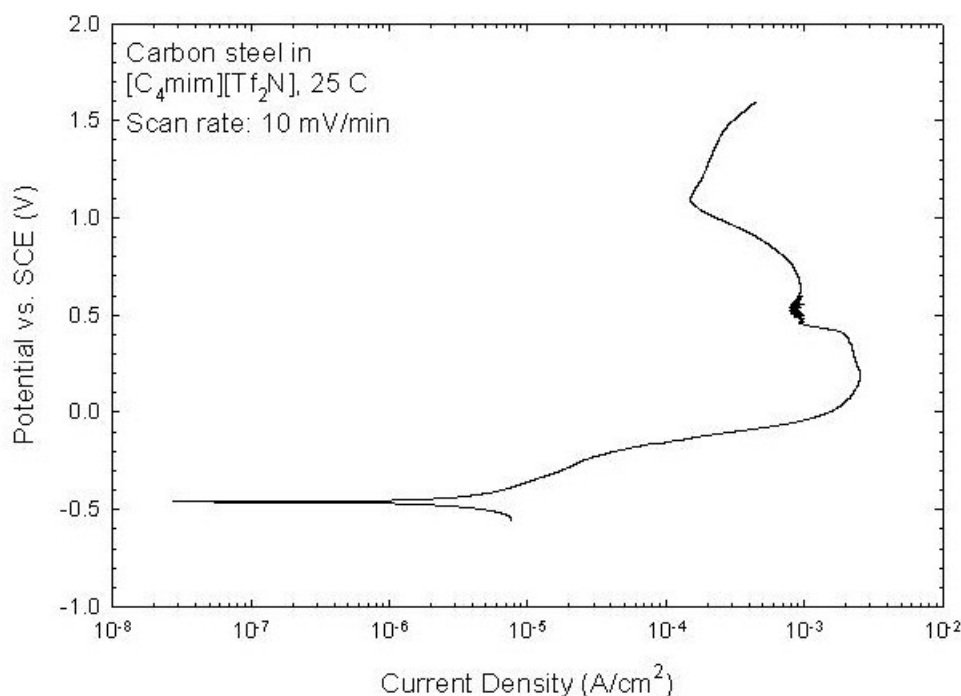


Figure 6. Potentiodynamic polarization plot of 1018 carbon steel in $[C_4mim]Tf_2N$ at 25 °C.

The potentiodynamic tests show that in $[C_4mim]Cl$ no stable passive films can be formed on stainless steel. Chloride restricts the stability of oxidized chromium films, leading to localized corrosion by film breakdown. Among the four ionic liquids tested, $[C_6mim]PF_6$ and $[C_8mim]PF_6$ showed relatively evident passivity. At high oxidizing potentials, the current densities in both $[C_6mim]PF_6$ and $[C_8mim]PF_6$ did not increase significantly. Therefore, the alloy may be resistant to localized corrosion at very high oxidizing potentials in these ionic liquids.

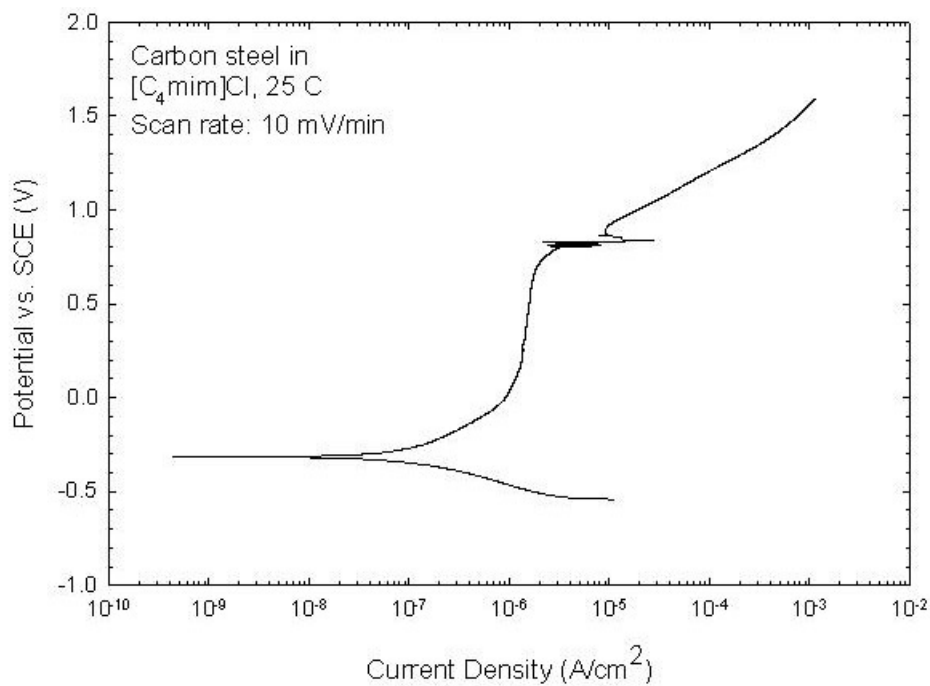


Figure 7. Potentiodynamic polarization plot of 1018 carbon steel in [C₄mim]Cl at 25 °C.

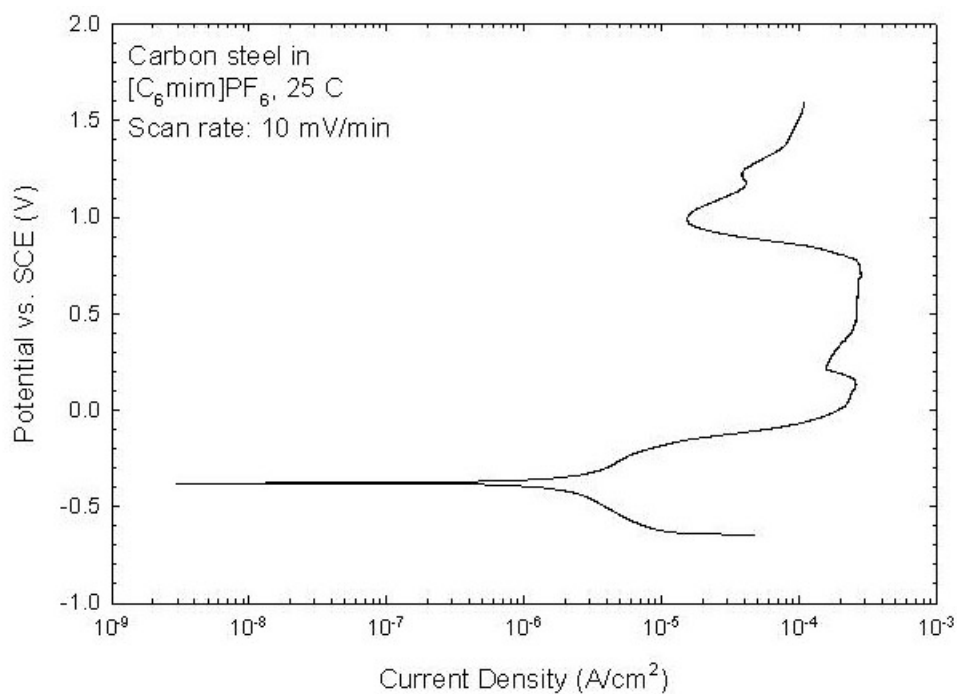


Figure 8. Potentiodynamic polarization plot of 1018 carbon steel in [C₆mim]PF₆ at 25 °C.

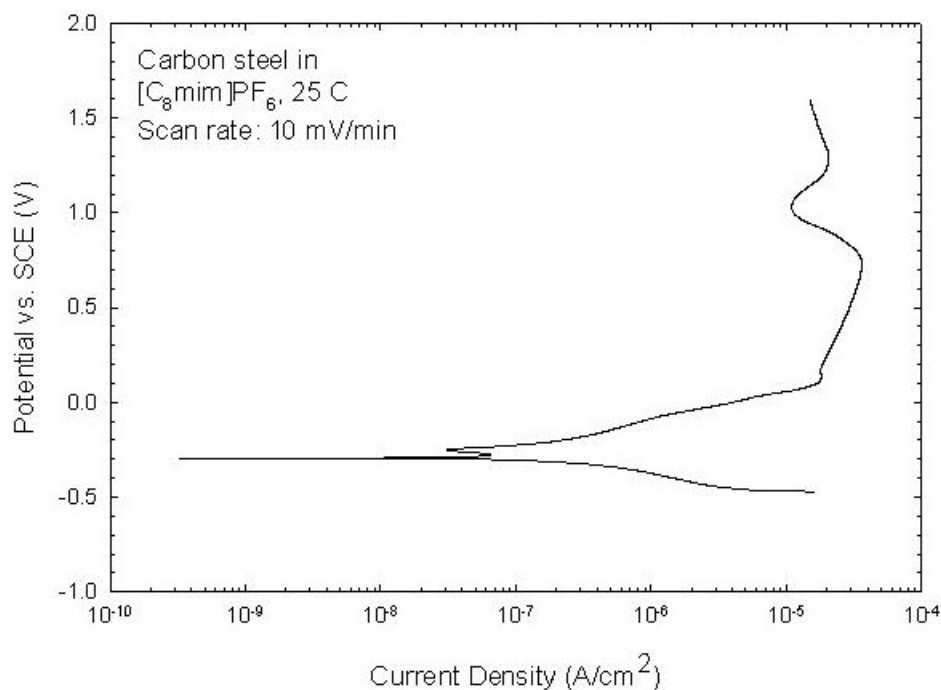


Figure 9. Potentiodynamic polarization plot of 1018 carbon steel in [C₈mim]PF₆ at 25 °C.

4. Conclusions

It has been found that 1018 carbon steel is outstanding in resisting uniform corrosion caused by the ionic liquids at room temperature. Corrosion rates ranging from 3-13 $\mu\text{m}/\text{yr}$ were obtained. The potentiodynamic tests showed in most cases an active/passive corrosion behavior. These tests also showed that ionic liquids containing chlorine ions prevent the formation of a stable passive film on 316 stainless steel. 1-alkyl-3-methylimidazolium hexafluorophosphate showed relatively evident passivity. This kind of ionic liquid may show better resistance to localized corrosion at very highly oxidizing potentials. Future studies are needed to evaluate the corrosion resistance of the alloy at higher temperatures.

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References

1. Y. You, E.J. Hu, *Appl. Therm. Eng.*, 22 (2002) 357.
2. G.C. Bakos, I. Ioannidis, N.F. Tsagas, I. Seftelis, *Appl. Energy*, 68 (2001) 43.
3. S.D. Odeh, G.L. Morrison, M. Behnia, *Solar Energy*, 62 (1998) 395.
4. J.E. Pacheco, S.K. Showalter, W.J. Kolb, *Proc. Solar Forum 2001 Solar Energy: The Power to Choose*, ASME, Washington, D.C., 2001 (in CD-ROM).
5. B. Wu, R.G. Reddy, R.D. Rogers, *Proc. Solar Forum 2001 Solar Energy: The Power to Choose*, ASME, Washington, D.C., 2001 (in CD-ROM).
6. V. Kamavaram and R. G. Reddy, *Electrochemical Studies of Aluminum Deposition in Ionic Liquids at Ambient Temperatures*, *Light Metals 2002*, W. Schneider (Editor), TMS, 2002, p. 253.
7. P. Wasserscheid, K.W. Keim, *Angew. Chem. Int. Ed.*, 39 (2000) 3773.
8. T. Welton, *Chem. Rev.*, 99 (1999) 2071.
9. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.*, 35 (1996) 1168.
10. Denny A. Jones, *Principles and Prevention of Corrosion*, 2nd Edition, Prentice-Hall, Inc., Upper Saddle River, NJ, 1996, p. 76.