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INFLUENCE OF WATER ON THE ANODIC OXIDATION MECHANISM OF DIETHYLENETRIAMINE (DETA) ON PLATINUM ELECTRODE

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ABSTRACT. Diethylenetriamine was oxidised in different electrolytes on platinum electrode. In non-aqueous electrolyte, an irreversible oxidation peak characteristic of DETA oxidation appears on the voltammogram followed by a constant current until the higher limit of the sweeping potential domain is attained. The following successive scans showed a high decrease of the current intensity and that is due to the formation of an insulating coating layer on the electrode surface. When water is added to the non-aqueous electrolyte, a DETA oxidation wave appears on the voltammograms. That oxidation wave is observed on the following scans. Indeed, DETA oxidation mechanism seems to be different either the electrolyte is free or not of water. In non-aqueous electrolyte, DETA oxidation leads to electrode surface covering by a thin polymeric film but in water containing electrolyte, oxygen evolution occurs and DETA oxidation leads to uncoated surface by producing aldehyde and amine through imine hydrolysis.

KEY WORDS: Non-aqueous electrolyte, Coating, Oxidation, Diethylenetriamine, Imine, Chelating agent, Cyclic voltammetry

INTRODUCTION

Surface coating layer has gained a great interest in many applications such as corrosion study [1-4], biological analysis, sensor fabrication, etc. Thus some fields of research have intensively studied the development of polymeric thin films like polypyrrole [5], polyaniline [6], polymer of thiophene or benzene derivatives [7-9] on different anode materials. Many other compounds possessing two amino groups such as ethylenediamine (EDA), triethylenediamine (TEDA), diethylenetriamine (DETA), and 5-amino indole (AMI) are known to interact strongly with surface atoms of many materials and they are used in acidic water as corrosion inhibitors acting by adsorption. The intermediates of solvent oxidation at an electrode as well as the passivation films formed onto electrodes are of importance for the fundamental understanding of electrochemical reactions as for protecting materials against corrosion [10, 11]. And due to primary polyamine electron rich nitrogen, it has gained great attention because it could be easily polymerized. Among primary polyamine varieties, diethylenetriamine (DETA) has kept our attention and has been used for this study. DETA contains two primary amines at both sides of its formula and a secondary amine between two ethylene groups. DETA is often used in the coordinated chemistry and favours metallic complexes formation in aqueous solution [12]. DETA is highly caustic, soluble in ethyl alcohol, in water and has almost the same physico-chemical properties like ammonia [11]. Due probably to its high causticity, its electrochemical oxidation is not too much investigated.

In this paper, we will focus on its electrochemical oxidation in different electrolyte in order to determine the better condition of its oxidation.

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EXPERIMENTAL

The chemicals diethylenetriamine ($NH_2CH_2CH_2NHCH_2CH_2NH_2$), lithium sulfonate trifluoromethane ($LiSO_3CF_3$), potassium hexafluorophosphate (KPF_6) were purchased from Aldrich.. They were used as received without further treatment. $LiSO_3CF_3$ and KPF_6 in solution act as supporting electrolyte.

The conductivity of the electrolytes was measured with a Meterlab conductimeter. The conductivity of the electrolytes was measured at 23 °C in the absence of water and at 49 °C in the presence of water.

The electrochemical measurements were carried out in a conventional three electrode cell at room temperature (25 °C) with an Autolab PGstat 20. The working electrode was a platinum wire. A spiral platinum wire was used as counter electrode and a silver wire (Ag/Ag^+) as reference electrode. All the potentials are referred to Ag.

The different measurements were made in a glovebox. The electrolytes were purged with nitrogen before measurements.

All the vessels were dried in an oven before used.

RESULTS AND DISCUSSION

Cyclic voltammetry of DETA in electrolyte free of $LiSO_3CF_3$ and in $LiSO_3CF_3$-water mixture

Figure 1 presents three successive cyclic voltammetry scans obtained in the DETA containing non-aqueous electrolyte. All the voltammograms show the same trends with no peak. The current seems to increase linearly with the potential. This observation indicates that DETA is not oxidized and the solution behaves like an ohmic conductor with a high calculated resistance value comprising between 180 kΩ and 300 kΩ.

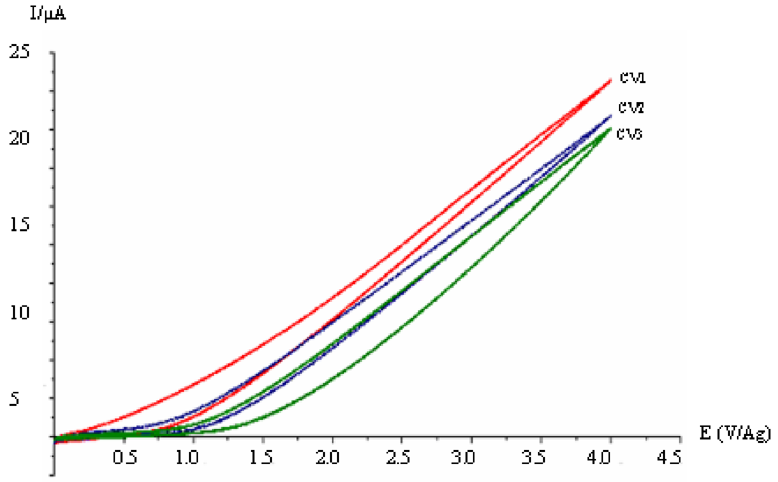

Figure 1. Cyclic voltammograms of DETA (4 M) in non aqueous solution free of $LiSO_3CF_3$ (5×10^{-2} M) on platinum electrode, 25 °C, 20 mV/s, successive scans: CV1 to CV3.

The cyclic voltammetry measurements investigated in the electrolyte made with the mixture of water (H_2O) and $LiSO_3CF_3$ without DETA are illustrated on Figure 2. This figure presents a potential domain where current intensity is almost equal to zero followed by a rapid increase in the current intensity with a very low variation of the potential. Indeed, that rapid increase in the current intensity could be due to an oxygen evolution reaction. The low value of current intensity in the whole anodic sweeping potential domain in solution of DETA free of $LiSO_3CF_3$ is linked to the low conductivity of DETA solution and its high ohmic resistance value. This low conductivity of DETA solution free of $LiSO_3CF_3$ is confirmed by experimental conductivity measurement given in Table 1.

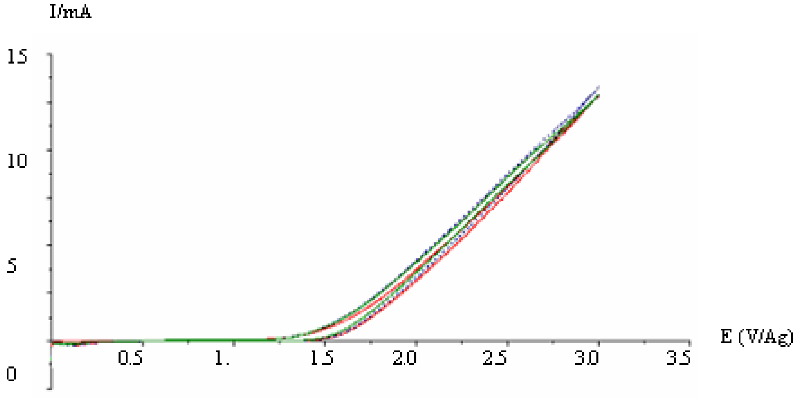

Figure 2. Cyclic voltammograms in H_2O-$LiSO_3CF_3$ electrolyte on platinum electrode, 25 °C, 20 mV/s, successive scans: CV1 to CV3.

Table 1. Conductivity of the DETA (4 M) containing electrolyte.

Electrolyte	Conductivity of the electrolyte (mS/m)
DETA (without supporting electrolyte) at 23 °C	0.123
DETA + Li(SO_3CF_3) 0.05 M at 23 °C	10.07
DETA + Li(SO_3CF_3) 0.05 M + H_2O at 49 °C	25

Cyclic voltammetry measurement in DETA-$LiSO_3CF_3$

In 0.05 M $LiSO_3CF_3$ containing DETA electrolyte, cyclic voltammetry measurements led to Figure 3. Three successive scans were made. On the first scan (Figure 3, CV1), the voltammogram presents an anodic current peak at ca. 1.25 V/Ag after that the current stays almost constant within the potential window investigated. After the higher limit of the applied potential window and in the backward of the scan, the current decreases rapidly and reached to almost zero value. No current peak is observed on the reverse scan of the voltammogram. On the second (Figure 3, CV2) and third scan (Figure 3, CV3), the current is lower than that obtained on the first scan. The forward and the reverse scan currents are closed to zero.

The anodic current peak observed in Figure 3 indicated the oxidation of DETA. The reaction occurs irreversible. The high decrease of the current after the first scan in the latter two scans indicated a passivation of the electrode surface. The fact that the current decreases too much indicated that the electrode surface passivation leads to the formation of an insulating coating layer on the electrode surface. From this result, it could be pointed out that the oxidation product of DETA adheres on the electrode surface and occupies the totally active site and makes further oxidation of the existing DETA molecule of the electrolyte impossible. The coat seemed to be stable as seen by the third scan response.

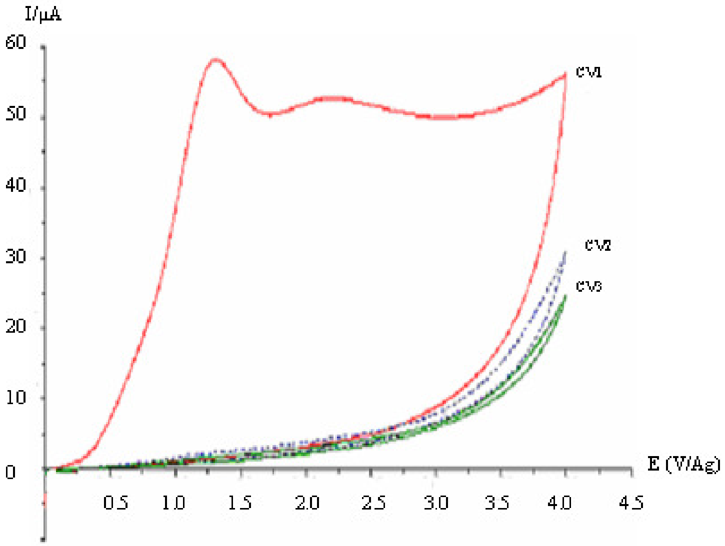

Figure 3. Cyclic voltammograms of DETA (4 M) on platinum electrode in presence of $LiSO_3CF_3$ (5×10^{-2} M), 25 °C, 20 mV/s, successive scans: CV1 to CV3.

Extending the sweeping potential window to high negative values, Figure 4 is obtained. In this figure, one can observe the same voltammogram feature as in Figure 3 in the positive domain of sweeping potential but in the negative domain, different cathodic and anodic peaks are observed (Figure 4, CV1). Four reduction peaks at the potential of -0.47 V/Ag, -0.91 V/Ag, -1.61 V/Ag and -2.4 V/Ag and oxidation peaks at -1.9 V/Ag, -1.5 V/Ag and -0.5 V/Ag are present. On the following second scan (Figure 4, CV2), one observes a low decrease of the anodic current peak and in the negative domain of the potential, a decrease of the peak intensity is observed. For a third sweep in the potential domain of 0 to 3 V/Ag (Figure 4, CV3), a high decrease of the current density reaching to almost zero value is observed.

In fact, this result indicates that sweeping in the negative domain of potential leads to the deposit (the coat) reduction. This indicates that the coat is destroyed under cathodic polarization therefore it is an unstable coating layer under this condition. That deposit reduction leads the electrode surface to be almost naked that's why at the second scan (Figure 4, CV2), the anodic current peak is observed. Such a result obtained using DETA is in accordance with that indicated in literature where the authors considered the departure of the coating layer under the cathodic polarization as a new electrode cleaning method in pure polyamine, ethylenediamine (EDA), electrolyte [13].

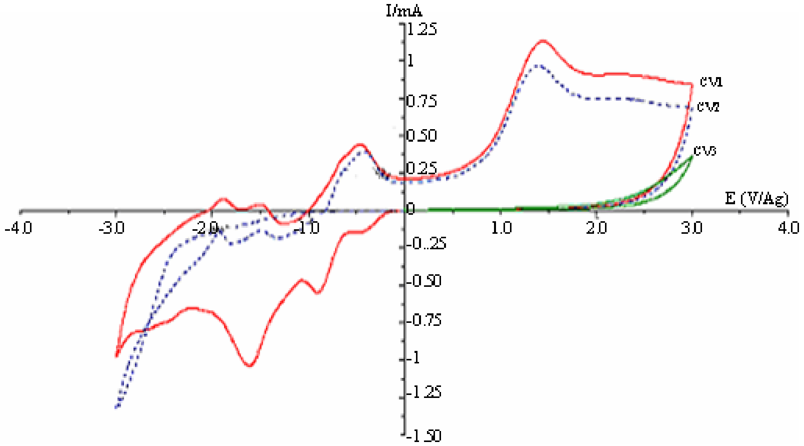

Figure 4. Cyclic voltammograms of DETA (4 M) in the potential domain from -3 V to 3 V on platinum electrode for the first two scans (CV1 and CV2) and the third (CV3) is made in the sweeping potential domain of 0 to 3 V/Ag, 25 °C, 20 mV/s.

Influence of different supporting electrolyte on DETA oxidation

Two supporting electrolytes KPF_6 and $LiSO_3CF_3$ have been used and the obtained results are presented in Figure 5.

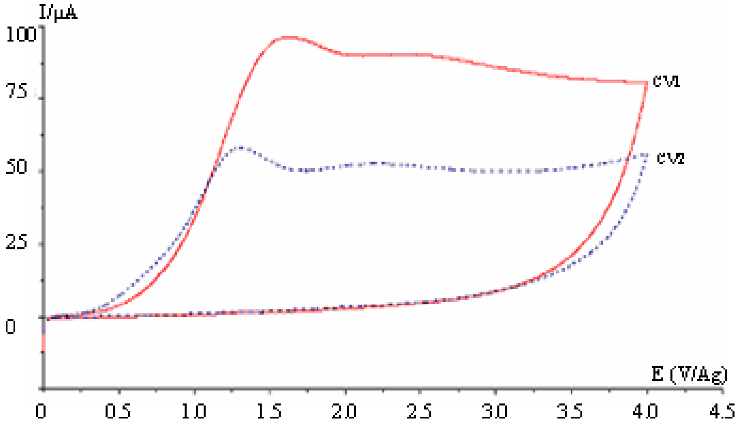

Figure 5. Influence of different supporting electrolytes on DETA (4 M) oxidation, 25 °C, 20 mV/s, (CV1): in presence of KPF_6 (5 x 10^{-2} M) and (CV2): in presence of $LiSO_3CF_3$ (5 x 10^{-2} M).

The voltammograms present the same shape. In the presence of KPF_6 (Figure 5, CV1), the anodic current peak characteristic of DETA oxidation is more important than that where

$LiSO_3CF_3$ (Figure 5, CV2) is used. Increasing the concentration of $LiSO_3CF_3$ leads the anodic current peak to increase (Figure 6).

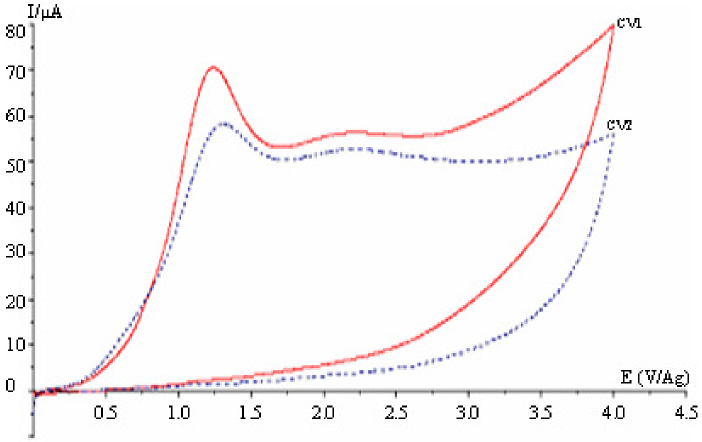

Figure 6. Influence of the concentration of $LiSO_3CF_3$ on DETA (4 M) oxidation, 25 °C, 20 mV/s, (CV1): in presence of $LiSO_3CF_3$ (10^{-1} M) and (CV2): in presence of $LiSO_3CF_3$ (5×10^{-2} M).

This result indicated that the supporting electrolyte such as KPF_6 (Figure 5, CV1) and $LiSO_3CF_3$ (Figure 5, CV2) lead to the same mechanism of DETA oxidation causing the electrode surface passivation. The fact that in the presence of KPF_6 (Figure 5, CV1) the current increases like that observed when the concentration of $LiSO_3CF_3$ (Figure 6) was increased revealed a high decrease of the electrolyte resistance with KPF_6. Indeed, KPF_6 and $LiSO_3CF_3$ in their dissociated forms, i.e. ions; contribute solely to the current transport in the electrolyte.

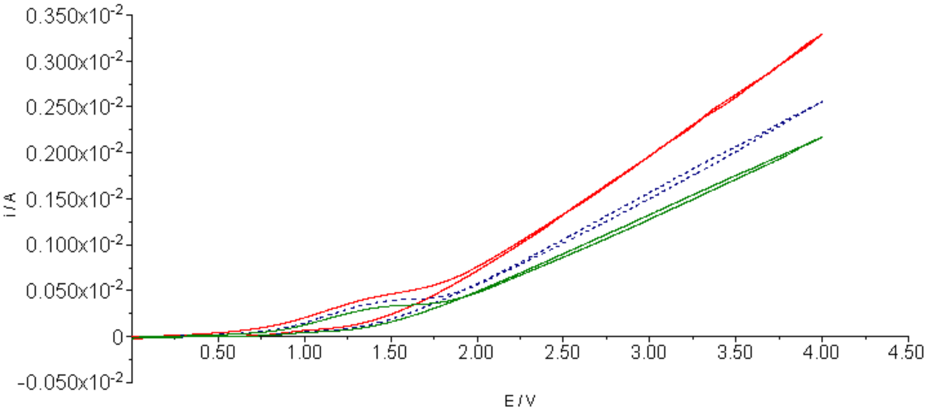

Figure 7. Cyclic voltammetry of DETA (4 M) electrolyte containing water (50 % of H_2O in the total electrolyte mixture), 20 mV/s, successive scans: CV1 to CV3.

Cyclic voltammetry in DETA-$LiSO_3CF_3$-water

Figure 7 shows the results obtained during cyclic voltammetry measurement in the electrolyte composed of the mixture of DETA-$LiSO_3CF_3$-H_2O. The different voltammograms in Figure 7 present the same shape from the first to the third voltammogram. Changing the water content i.e. 15 %, 30 % and 50 % of water in the total electrolyte mixture, the voltammograms gave almost the same feature (not presented here). In the potential domain from 0.5 V/Ag to 1.75 V/Ag (Figure 7), an anodic oxidation wave is observed in the voltammograms. At potential values higher than 1.75 V/Ag, the current increases rapidly and linearly with the potential.

This observation indicates that in the presence of water, the oxidation of DETA occurs differently than that made in non-aqueous electrolyte. This could be due to the hydrolysis of DETA oxidation product.

Conductivity measurement of the electrolyte

The conductivities of different electrolytes are given in Table 1. It is shown that the conductivity of DETA without supporting electrolyte was very low. It increases in the presence of $LiSO_3CF_3$. In the mixture of DETA-$LiSO_3CF_3$-H_2O with water a high conductivity value is observed and an exothermic reaction occurs.

DETA oxidation mechanism in the used electrolytes (DETA-$LiSO_3CF_3$ electrolyte with or without water)

Due to electron-rich DETA containing nitrogen on both sides, its oxidation is supposed to occur by releasing solvated electron as below [13, 14]

$$R\text{-}NH_2 \rightarrow R\text{-}NH_2^+ + e^-_{\text{solvated}} \tag{1}$$

In the presence of water in the mixture DETA-$LiSO_3CF_3$, no passivation of the platinum surface was observed. In fact, in this medium the oxidation product undergoes hydrolysis to form aldehydes and amine [15, 16]. That is the case when ethylenediamine (EDA) is oxidized in the presence of moisture [13]. This phenomenon has been observed in earlier work during simple imine reduction in aqueous electrolytes [15, 17].

In the water containing electrolyte, DETA oxidation can be described according to the mechanism below where DETA oxidation leads to imine after solvated electron releasing and deprotonation. And then imine is hydrolysed to aldehydes and ammonium ion (Figure 8). And also, in presence of water, a side reaction such as oxygen evolution due to water decomposition according to the following equation (2) occurs. Such a reaction limits the DETA oxidation potential domain and the gas evolvement hampers DETA oxidation product to adsorb on the electrode surface.

$$2H_2O \leftrightarrow 4H^+ + 4e^- + O_2 \tag{2}$$

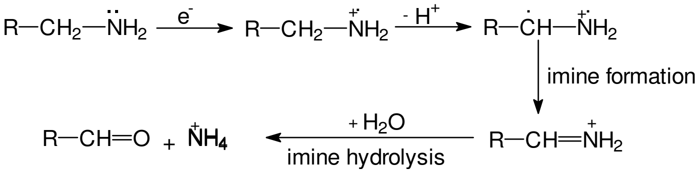

Figure 8. Mechanism of DETA oxidation in water containing non-aqueous electrolyte.

In electrolyte free of water, DETA oxidation leads to an oxidation product that covers the electrode surface. In fact, when DETA is oxidizing, after solvated electron releasing, there is a departure of NH_2 group causing the formation of carbocation with high reactivity. The carbocation is stabilized due to the causticity of the electrolyte [18]. Then, that carbocation reacts with the terminated amine of the existing DETA molecules of the electrolyte. By hydrogen bonds between oxygen existing on the electrode surface and hydrogen from amine group, the DETA oxidation product is grafted or hardly adsorbed on the electrode surface. The proposed oxidation mechanism of DETA in non-aqueous electrolyte is given in Figure 9. This oxidation leads to a polyethyleneimine-like coating [19]. That passivation seems to occur when the polyamine possesses two primary amines at both sides in the structure of the molecule [19]. The coated electrode can be used for the detection of metallic ions and for solution pH measurement due the polyethyleneimine selectivity properties [18].

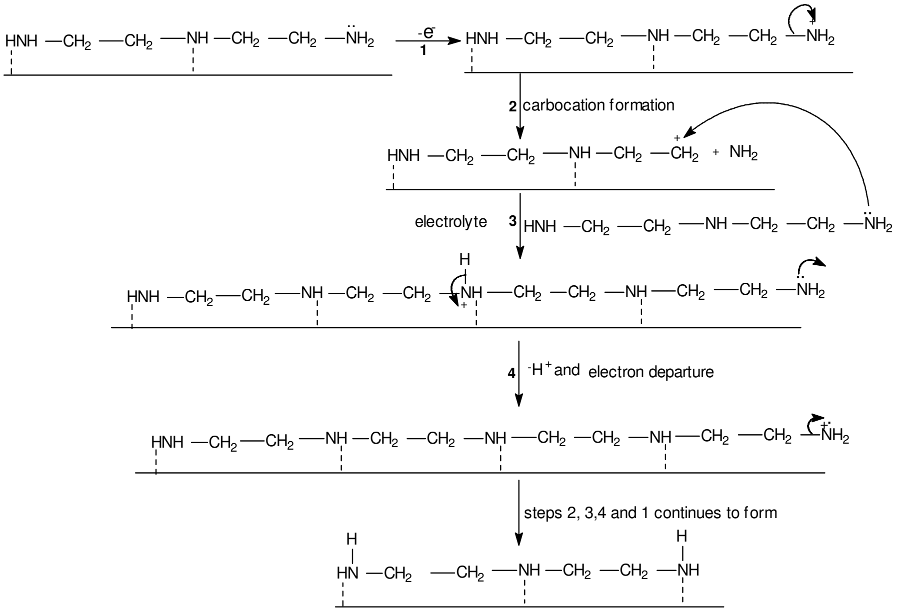

Figure 9. Mechanism of DETA oxidation in non-aqueous electrolyte.

CONCLUSION

DETA oxidation is possible in the two electrolytes investigated (DETA-$LiSO_3CF_3$ and DETA-$LiSO_3CF_3$-H_2O). This work has pointed out that the presence of water in the second electrolyte makes the DETA oxidation mechanism to be different to that made in a pure non-aqueous electrolyte. To perform DETA oxidation, KPF_6 and $LiSO_3CF_3$ can be used and they considerably increase DETA solution conductivity. In the DETA-$LiSO_3CF_3$-H_2O, DETA oxidation leads to the formation of an unstable imine, which is further hydrolysed to aldehyde and ammonium ion. A side reaction, such as oxygen evolution, occurs also in that medium limiting DETA oxidation potential domain and hampering DETA oxidation product to adsorb on the electrode surface. But in DETA-$LiSO_3CF_3$, DETA oxidation leads to the formation of an insulating coating layer (polymeric film) on the electrode surface. That film is destroyed in the negative potential domain by reduction leading to a cleaned electrode surface.

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