Research Article

EFFECT OF SOLVENT AND TEMPERATURE ON THE KINETICS OF ANODIC OXIDE FILMS FORMED ON NIOBIUM IN 0.1 M FERROUS AMMONIUM SULPHATE: SURFACE MORPHOLOGY BY SEM STUDIES

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ABSTRACT
The kinetics of anodic oxidation of Niobium in 0.1M Ferrous ammonium sulphate has been studied under galvanostatic conditions (at a constant current density of 8mA.cm^{-2}) and at room temperature. The plots of formation voltage vs time and reciprocal capacitance vs time were drawn and from these plots, kinetic results - formation rate, current efficiency and differential field were calculated. These results have been improved with the addition of solvent (ethylene glycol at various concentrations) to the aqueous solution of 0.1M ferrous ammonium sulphate. Kinetics of film formation was also studied at different temperatures ranging from 273K to 333K by using galvanostatic conditions. It was observed that kinetic results were found to be increased linearly with the decrease in temperature. The surface morphology of the anodic films was also studied by Scanning Electron Microscopy and the morphology of the anodic films was compared.

Keywords: Anodic oxidation, ferrous ammonium sulphate, surface morphology.

1. INTRODUCTION

The metals such as Niobium, Zirconium (& its alloys), Tantalum and Aluminium can be anodized to give thin, uniform and relatively flaw free oxide films, which are stable chemically & mechanically. Anodic oxide films formed on niobium are corrosion resistant, generally much stronger and more adherent than most types of paint and metal plating. These anodic films are also useful in the field of electronic & electrical components. Photo effect and photoconduction on these films formed on Nb, Ta, Ti, Al in the systems metal/metal oxide/electrolyte were investigated by Young[1], Schmidt et al[2], Sasaky[3],

& Ruprecht[4]. Many other applications have been reviewed by Aladjem[5].
In the present work, the kinetics of anodization on niobium in aqueous solution of 0.1M Ferrous ammonium sulphate and aquo-glycolic media in various proportions (v/v) of water – ethylene glycol mixtures ranging from 0 to 75% ethylene glycol are studied. An attempt was also made to study the kinetics at various temperatures ranging from 273K to 333K under galvanostatic conditions (at a constant current density of 8mA.cm^{-2}).Surface morphology of the anodic films formed at different anodic conditions is

compared & studied by Scanning Electron Microscopy.

2. MATERIALS AND METHODS

Niobium was of 99.5% purity, supplied in the form of annealed sheet by NFC, Hyderabad as gift samples. In the present work, the foil samples used were cut with the aid of a punch into flag shaped specimens of $1cm^2$ working area on both sides & 2cm long tag. The chemical polishing mixture for niobium is 5:5:1.5 by volume 53% HNO_3, 49% HF, 98% H_2SO_4.

For anodizing, a closed shell of 200 mL capacity was used. The cathode used was a platinum foil of $20cm^2$ superficial area to make double layer capacitance as large as possible. Electrolytes used were 0.1M Ferrous ammonium sulphate in 25, 50 and 75% aquo-glycolic mixtures, the solvent being Ethylene glycol.

The temperatures used in the current study were ranging from 273K to 333K.

All the experiments were carried out at a constant current density of 8 $mA.cm^{-2}$. The experimental procedure for the anodization is given elsewhere[6]. The kinetic results calculated are formation rate in Vs^{-1}, current efficiency (η) % and differential fields of formation (FD) in MV cm^{-1} from the conventional plots V vs. t, 1/C vs. t and 1/C vs V.

The surface morphology of the anodic film was examined using Scanning Electron microscope (SEM). The SEM's were taken at IICT, CSIR, Hyderabad.

The surface was thoroughly rinsed with distilled water and dried under infrared lamp and cleaned gently with fine tissue paper. The surface was coated with gold, Palladium conducting material using evaporation technique and signal processed secondary electron images were taken from scanning electron microscope model SEM Hitachi- S520 at 10 KV, Hitachi instruments made in Japan (Oxford link ISIS-300 UK).

3. RESULTS AND DISCUSSION

Anodization of Niobium in 0.1M ferrous ammonium sulphate was carried out at a constant current density of 8 $mA.cm^{-2}$ and at room temperature. The plots of formation voltage vs time and reciprocal capacitance vs time were drawn and kinetic results were calculated.

3.1 Effect of Solvent

In the current study, anodization of niobium in 0.1 M ferrous ammonium sulphate was performed by mixing various proportions of ethylene glycol (v/v 25, 50 & 75%) to the aqueous solution. There was an improvement in the kinetics of film formation as given in Table 1. The relevant plots are shown in Figures 1& 2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors[7]. These facts support the current results shown in Table 1. This can be explained on the basis of decrease in the dielectric constant of the medium as shown in Table 2.

In solutions of low dielectric constant there is less chance of ion-dipole interactions (solvent–ion interactions) which do not interfere in the oxide film formation. However the ions in the high dielectric constant solutions interact with oxide ions responsible for oxide film formation due to high solvation with water molecules. In such solutions, the kinetics are poor. The kinetics are better in low dielectric constant solutions for 25, 50, & 75 % aquo-glycolic media, the dielectric constant values are low leading to a marked improvement in the kinetics.

3.2 Scanning Electron Microscopy

The surface morphology of the films was studied and compared by scanning electron migroscopy. Figure 3 and Figure 4 are the scanning electron micrographs of anodic films formed on Niobium in aqueous and aquo-glycolic solutions of 0.1M Ferrous ammonium sulphate upto 200V.

When compared, the roughness & non uniformity of the surface are decreased when electrolytic medium is changed from aqueous to aquo-glycolic medium (Figure 4) is observed to be smoother than the film formed in aqueous medium (Figure 3)

Vermilyea studied the formation of anodic films on tantalum in aqueous[8] and non-aqueous[9] solutions. He suggested that the composition of film depends on the solution in which it is formed.

Nageshwar rao et al.[10] observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic.

Vermilyea[9] reported that the optical thickness was smaller in the non-aqueous solutions and the increase in weight for a given charge passed could be as much as twice that expected.

Moshashi Koyama[11] carried out anodization of titanium in non-aqueous media and confirmed that the oxide film consists of double layers and suitable for electrolytic capacitors.

Wei Wei et al.[12] reported the growth of layers by anodization of tantalum in a non-aqueous electrolyte consisting of an optimized

glycerol/ethylene glycol mixture with the addition of NH_4F

Schmidt et al.[13] observed that the layers of TiO_2 obtained in non-aqueous electrolytes are much adherent and uniform than those realized in aqueous media.

Climent Montoliu et al. [14] studied the anodization of titanium in acid, alkali and neutral baths (aqueous and aquoglycolic) and suggested from the structure and dielectric properties, that the anodic coatings formed in non-aqueous media acts as better dielectric capacitors.

Panasa Reddy et al.[15] and Lavanya et al.[16] also studied in trisodium citrate, 0.1 M KOH (aquo-glycolic) respectively and found that the breakdown voltage was higher when anodized in ethylene glycol medium. This was also supported by other worker [17].

3.3 Effect of Temperature

Another attempt was also made to study the effect of temperature on the anodization of niobium in 0.1 M ferrous ammonium sulphate at a constant current density of 8 $mA.cm^{-2}$. Anodizations were carried out on Niobium at various temperatures ranging from 273K to 333K. The conventional plots were drawn as shown in the Figures 5 & 6.

From these plots, the kinetic results were calculated. It was observed that the formation rate, current efficiency, differential field & break down voltage were found to be increasing linearly with the decrease in temperature as shown in Table 3.

The decrease in the field, formation rate & Breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

Temperature[18] was found to exert a marked influence on th anodizing characteristics of Nb & Zr

Nigam et al[19] studied anodic growth of films on tantalum in aqueous solutions of citric acid& oxalic acid at different temperatures.

Colton & Wood[20] reported that the BDV was decreased with increase in temperature in the case of titanium oxide films and explained the observation on the basis of dissolution of the film.

Bhaskar reddy et al [21] observed the similar trend of decreasing kinetic results with increase in temperature in 0.1M potassium tartarate.

The same results were observed by many others[22-28].

3.4 Scanning Electron Microscopy

The surface morphology of the films was studied and compared by scanning electron migroscopy. Figure 3 and Figure 7 are the scanning electron micrographs of anodic films formed on Niobium in aqueous solutions of 0.1M Ferrous ammonium sulphate at room temperature (273K) and at high temperature (333K) respectively. When compared, the film surface is rough & non- uniform with dissolution of oxide film at higher temperature (Figure 7)

4. CONCLUSIONS

The kinetics of film formation on Niobium in 0.1 M Ferrous ammonium sulphate have been improved by adding ethylene glycol to the aqueous solution and it is observed that the peak voltage, formation rate, current efficiency are increased but differential field of formation decreased with the glycol content of solution. This can be attributed to the decrease in the dielectric constant of the solution with the increase in glycol content of the solution.

It was also observed that the kinetics were good at low temperatures. It was observed that the formation rate, current efficiency, differential field & break down voltage were found to be increasing linearly with the decrease in temperature. The decrease in the field, formation rate & Breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

Table 1: Anodic films formed on Niobium in 0.1M Ferrous ammonium sulphate both aqueous and aquo-glycolic-media

Percentage of Glycol	Formation Rate, dV/dt $(V.s^{-1})$	Current efficiency, η (%)	Differential field,F_D $(MV.cm^{-1})$
0	2.09	73.80	5.59
25	2.20	82.10	5.30
50	2.33	88.00	5.22
75	2.42	94.30	5.06

Table 2: Variation of Dielectric constant as a function of time in aquo-glycolic solution

EG (%)	0	20	40	60	80	100
Dielectric constant	80.0	72.8	69.2	57.8	43.2	37.7

Table 3: Anodic films formed on Niobium in 0.1M Ferrous ammonium sulphate at different temperatures

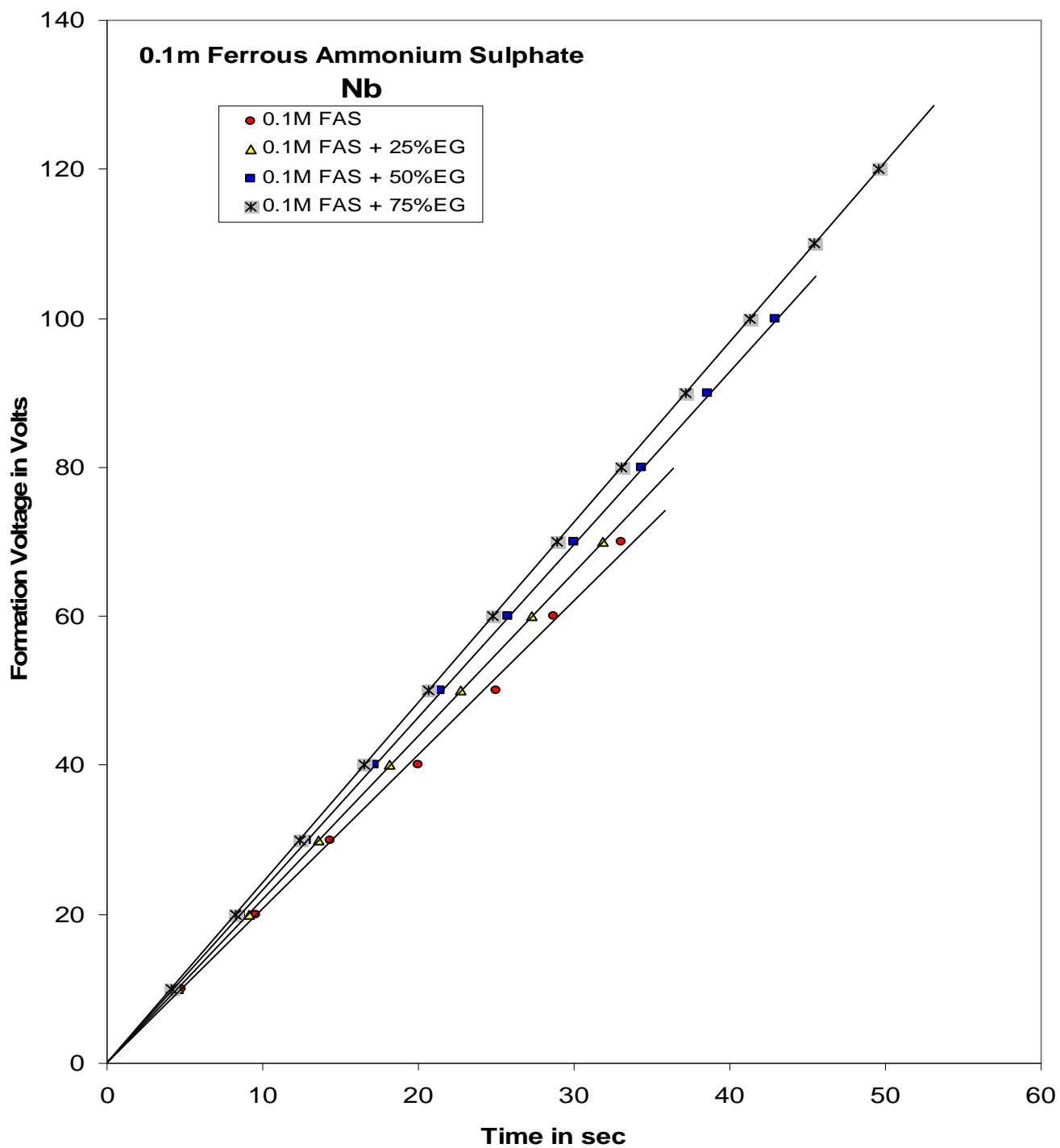| Temperature ,T (K)	Formation rate,dV/dt $(V.s^{-1})$	Current efficiency, η (%)	Differential field, F_D $(MV.cm^{-1})$	Break down voltage (V_B) , Volts
273	2.31	80.26	5.69	230
288	2.16	76.52	5.60	217
303	2.06	73.00	5.59	201
318	1.89	68.73	5.46	178
333	1.64	60.35	5.38	148

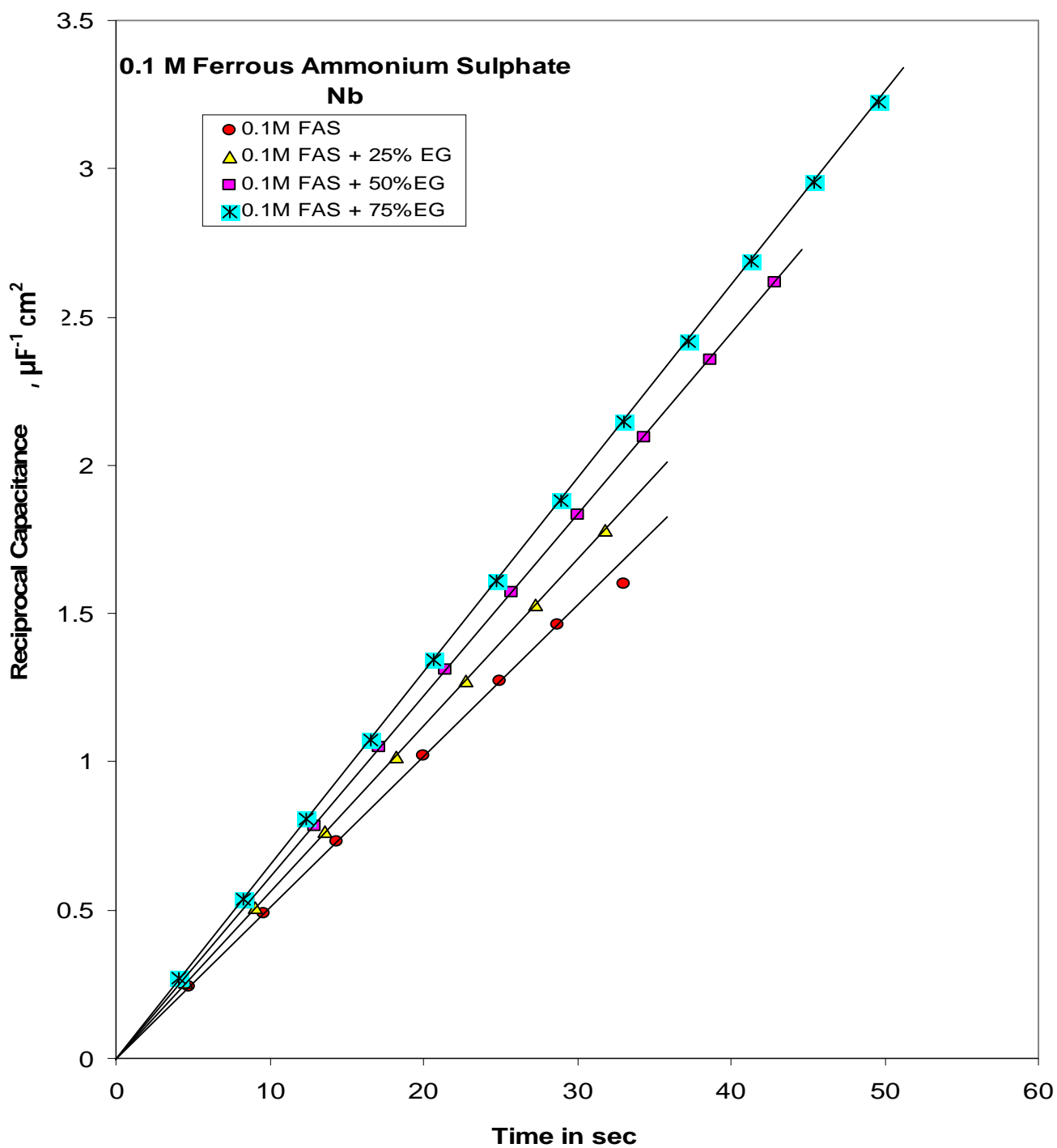**Fig. 1: Plot of formation voltage as a function of time in aquo-glycolic solution**

Fig. 2: Plot of reciprocal capacitance as a function of time in aquo-glycolic solution
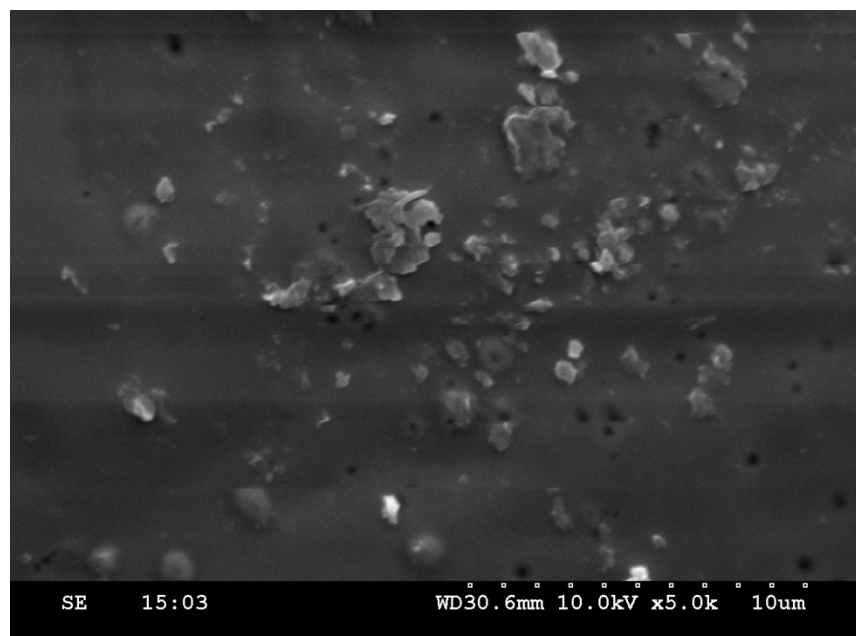
Fig. 3: SEM of the film formed upto 220V on Nb in 0.1M ferrous ammonium sulphate (aqueous medium) at room temperature (Magnification of the micrograph is X 5000)
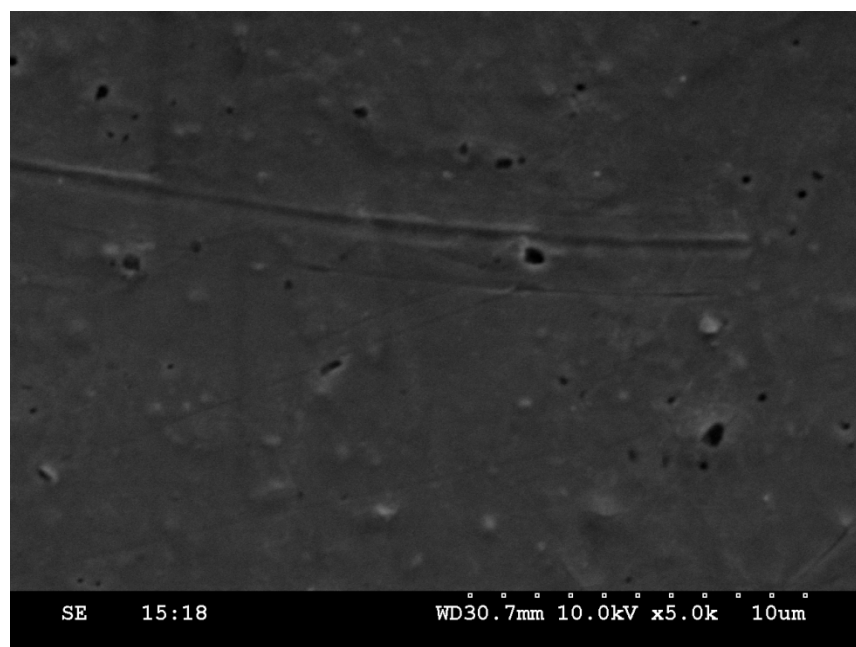

Fig. 4: SEM of the film formed upto 220V on Nb in 0.1M ferrous ammonium sulphate (75% glycolic medium) at room temperature (Magnification of the micrograph is X 5000)
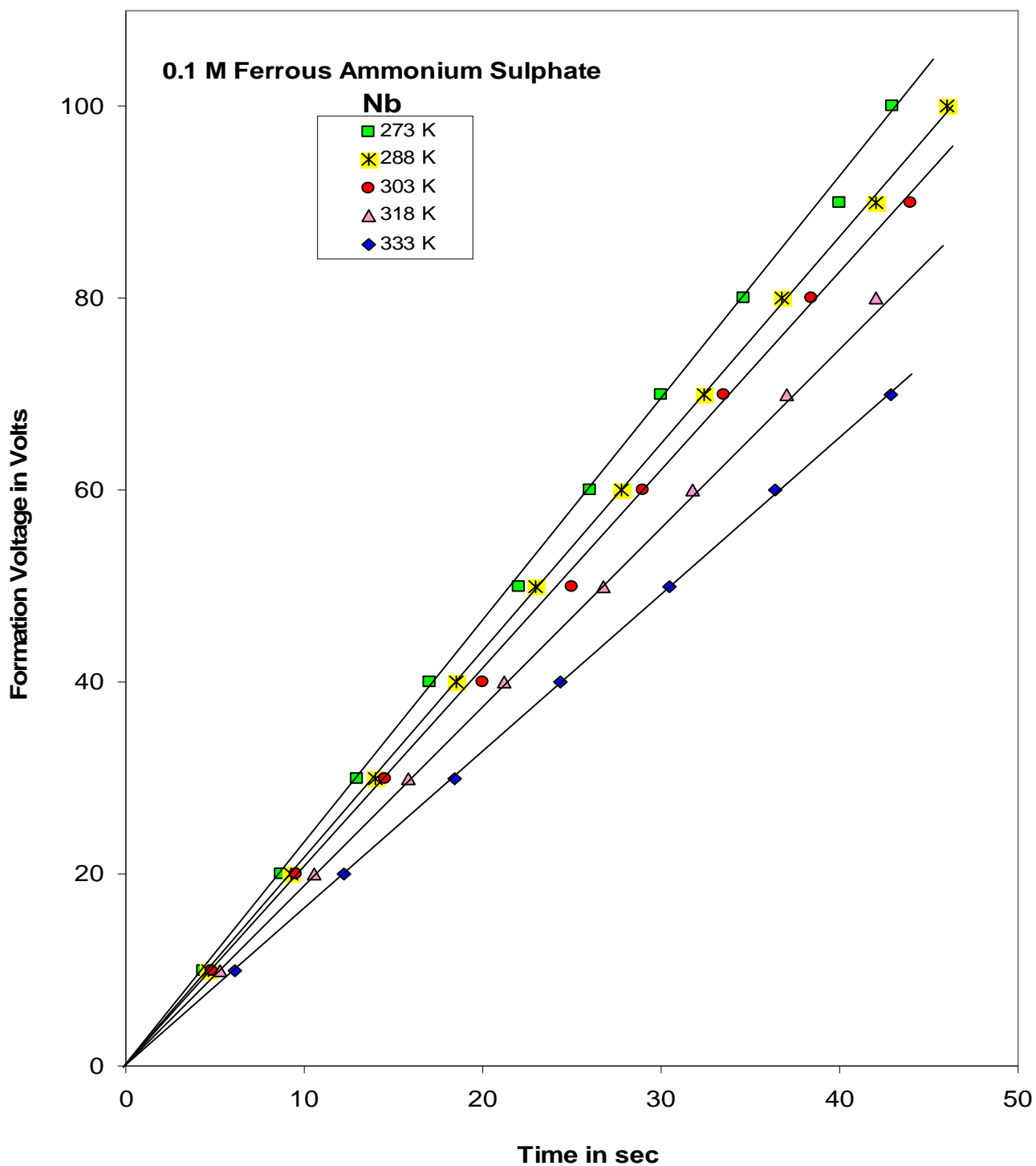
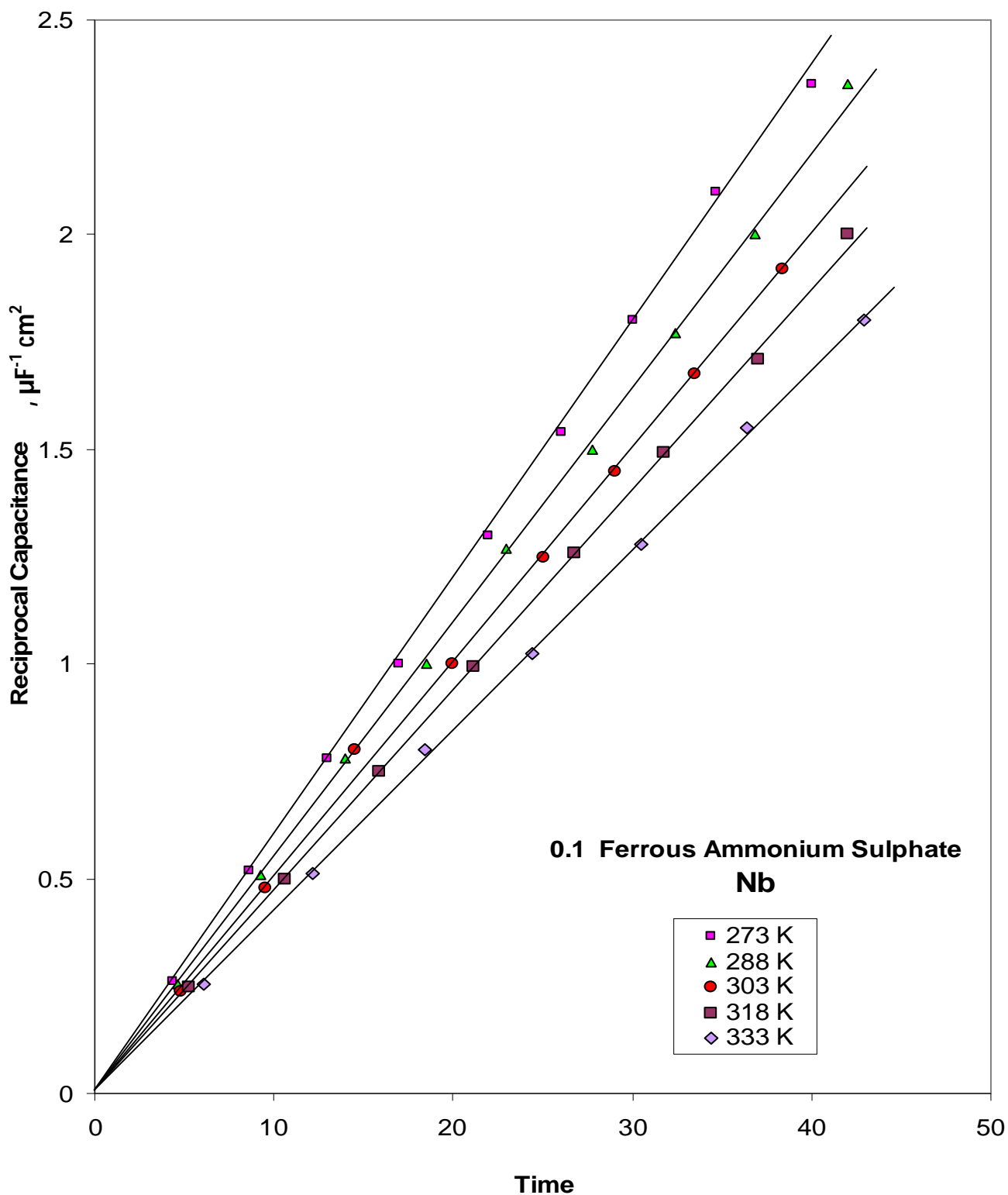**Fig. 5: Plot of formation voltage as a function of time at different temperatures**

Fig. 6: Plot of Reciprocal Capacitance as a function of time at different temperatures
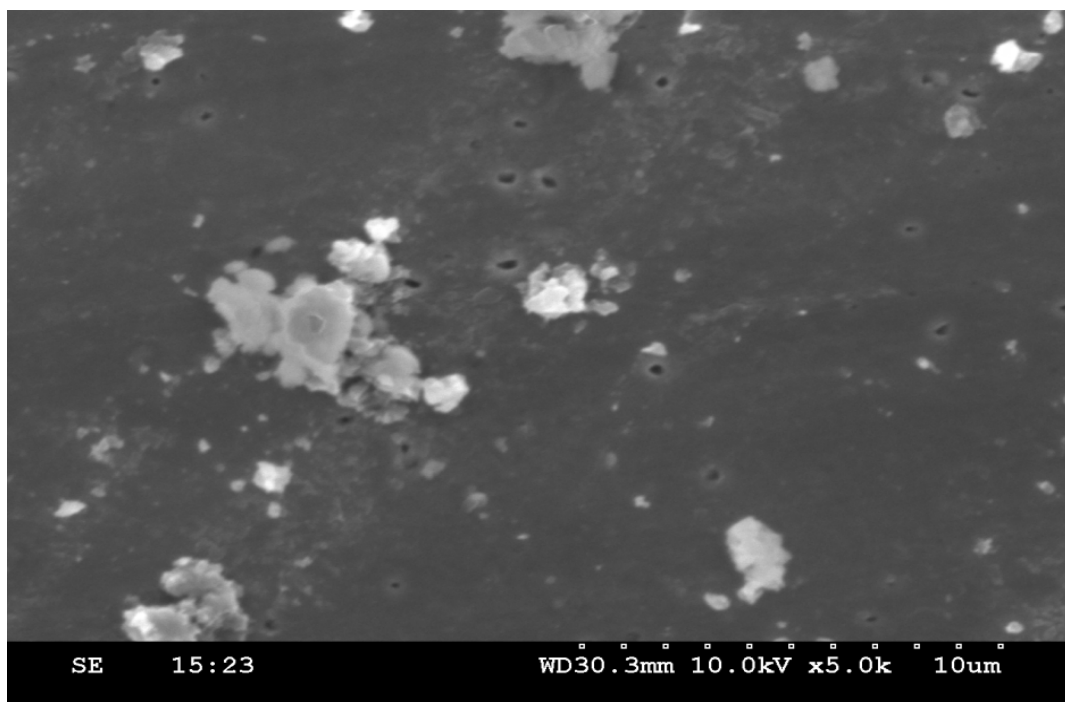
Fig. 7: SEM of the film formed on Nb upto 200V in 0.1M ferrous ammonium sulphate at higher temperature (331K)

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