

# A comparative evaluation on the anodic behavior of Cu and Ag electrodes in non-aqueous fluoride and fluoroborate media

V. Suryanarayanan · M. Noel

Received: 30 September 2008 / Revised: 10 November 2008 / Accepted: 15 December 2008 / Published online: 7 January 2009  
© Springer-Verlag 2008

**Abstract** The voltammetric responses of copper and silver had been extensively studied and compared in a variety of non-aqueous solvents such as acetonitrile (AN), propylene carbonate (PC) and sulfolane containing two different supporting electrolytes namely triethylamine-trishydrogen fluoride (TEA.3HF) and tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>). The dissolution rate and surface transformation on the electrode surfaces as a result of anodic polarization was investigated using atomic absorption spectroscopy (AAS) and scanning electron microscopy (SEM), respectively. In solvent-free TEA.3HF medium, the copper electrode shows high charge recovery ratio ( $Q_c/Q_a$ ), and the difference between the initial anodic and cathodic potentials, obtained at a current density of 2 mA cm<sup>-2</sup>, is around 0.11 V, suggesting that in this medium, Cu can certainly serve as reference electrode. On the other hand, on Ag electrode, substantial dissolution was observed leading to very high anodic ( $Q_a$ ) and cathodic ( $Q_c$ ) charges, and the surface morphology after the cyclic polarization results in roughened surface with large pores. The effects of incorporating AN and water as additives in TEA.3HF on the solubility and stability of these metal fluoride films are also reported. The dissolution pattern and film formation behavior of these two metals in the different solvents containing fluoride and fluoroborate ionic species have several qualitative similarities, as noted from cyclic voltammetry responses and SEM morphology. Anodic dissolution and precipitation process for both Cu and Ag depends significantly on the

nature of supporting electrolytes as well as solvents. In AN containing 0.1 M TEA.3HF, the dissolution of Cu and Ag electrodes was very high. Fluoride salts of Cu show lesser solubility than Ag in those solvents, while fluoroborate salts exhibit the reverse trend. The AAS data suggest that for a particular salt, which may be either fluoride or fluoroborate of Cu and Ag, the relative solubility decreases in the order AN > PC > sulfolane.

**Keywords** Anodic behavior · Cu dissolution · Ag dissolution · Fluoride and fluoroborate anions

## Introduction

Among the different molten fluoride media employed in many electrochemical systems, the study of electrode materials in KF-2HF melt presents challenging problems of a different kind in the corrosion field on account of the special properties of such media [1]. The reversible redox behavior of Cu/CuF<sub>2</sub> couple and the corrosion behavior of Cu and Mg had been extensively investigated in KF-2HF melt [2, 3]. Studies on the anodic behavior of Cu and Ni in KF-2HF melt revealed that the resistivity of the passive film on Cu was high, whereas the passive film on Ni was quite conductive and prevents Ni dissolution [4]. The electrode potentials of chemically and electrochemically prepared Cu/CuF<sub>2</sub>, Cu/CuF, Fe/FeF<sub>2</sub>, and Fe/FeF<sub>3</sub> films in the above melt were also analyzed thermodynamically in a recent work [5]. There are, however, only very few investigations of anodic behavior of Cu in other molten fluoride media. Electrochemical behavior of Cu in NH<sub>4</sub>HF<sub>2</sub>-HF was quite similar to that in KF-2HF melt. [6]. In SbF<sub>5</sub>-HF super acid medium, Cu had only little stability [7]. The nature of surface-bound CuF<sub>2</sub> film in anhydrous hydrogen fluoride (AHF)/hexafluorobutanol me-

V. Suryanarayanan (✉) · M. Noel  
Electro Organic Division, Central Electrochemical Research  
Institute,  
Karaikudi 630 006, India  
e-mail: vidhyasur@yahoo.co.in

dium was characterized using X-ray photoelectron spectroscopy [8]. The electrochemical behavior of Cu in triethylamine trisulphur fluoride (TEA.3HF) medium was compared with Ni and Ag [9].

On contrary, studies on the electrochemical behavior of silver in fluoride medium have received less attention. An electrochemical study of Ag in super acid HF + SbF<sub>5</sub> shows that Ag is not oxidized and that the couple Ag/Ag(I) may be used as reference electrode in this medium. [10]. In TEA.3HF, Ag was less stable than that of Cu [9]. A brief report on the effect of TEA.3HF ratio on the voltammetric behavior of Ag is also available [11]. The growth of AgX (X = F, Cl, Br and I) adlayers on Ag surface was characterized using atomic force microscopy [12].

Many fluoride-containing solvent supporting electrolyte systems are being investigated in recent times because of their industrial importance. Propylene carbonate (PC) containing fluoro anions, for example, LiPF<sub>6</sub> and LiBF<sub>4</sub>, are employed in Li batteries [13, 14]. Neat TEA.3HF as well as solvents such as PC, sulfolane, and acetonitrile (AN) containing TEA.3HF and tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) are currently employed in selective electro fluorination process [15, 16]. It would be worthwhile to search for a stable and reversible metal fluoride film, which can act as reference electrodes in such diverse non-aqueous fluoride media. In order to achieve this goal, the electrochemical behavior of Cu and Ag in different solvents such as PC, sulfolane, and AN containing two different fluoride media, namely, TEA.3HF and TBABF<sub>4</sub>, is examined comparatively in the present work.

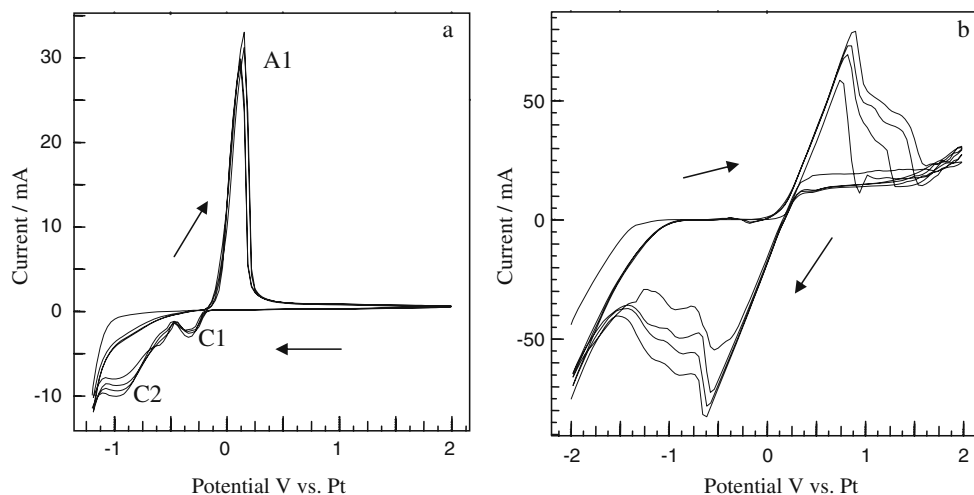
## Experimental

TEA.3HF was prepared by mixing TEA with freshly taken AHF (TANFAC, India) at the temperature range of freezing

mixture, evaluating the HF content by titration and adjusting the TEA.3HF ratio accordingly [9]. A polypropylene undivided cell containing Cu as well as Ag foil as working electrodes and Pt wire and Pt foil as quasi reference and counter electrode, respectively, was used in the present voltammetric investigations. Preliminary voltammetric experiments employing Cu and Ag rod as working electrodes in such fluoride media indicated some difficulties in achieving the reproducibility where very high anodic dissolution was noticed. Hence, fresh Cu (0.49 cm<sup>2</sup>) and Ag electrodes (0.31 cm<sup>2</sup>) were used for each experiment. A Pt foil (3 cm<sup>2</sup>) served as the counter electrode. An undivided cell was used throughout the experiments. The choice of reference electrode posed some problems. The palladium (Pd/H<sub>2</sub>) electrode showed instability, especially in TEA.3HF in which Pd dissolution was noticed. Hence, a Pt wire was used as a quasi-reference electrode in both supporting electrolytes. The measurements suggested that the Pt quasi reference potential in TEA.3HF is always close to the Pd/H<sub>2</sub> reference electrode within the limit of ±20 to ±30 mV. The reference potential, however, was checked from time to time externally against a saturated calomel electrode.

Acetonitrile (high-performance liquid chromatography grade), propylene carbonate (analytical reagent (AR) grade), sulfolane (AR grade), and triple-distilled water were used as solvents. Tetrabutylammonium tetrafluoroborate was obtained from Merck and used as such. Voltammograms were recorded in BAS-IM6 system under computer control with Thales USB 3.18 software, and anodic as well as cathodic charges were calculated using the above software. Scanning electron microscopy (SEM) was performed with JEOL, model 30CF instrument. The amount of Cu<sup>2+</sup> and Ag<sup>+</sup> species dissolved in the electrolyte was estimated using atomic absorption spectroscopy (AAS, GBC 906 AA, Australia). For the AAS analysis, Cu and

**Fig. 1** Multi sweep cyclic voltammograms of (a) Cu and (b) Ag in neat TEA.3HF at a sweep rate of 40 mV s<sup>-1</sup>. Number of cycles=4



**Table 1** Voltammetric characteristics of Cu and Ag electrodes obtained in different additives and solvents containing fluoride ions

Electrolyte	Electrode	$E_{ia}$ (V) <sup>a</sup>	$E_{ic}$ (V) <sup>a</sup>	$Q_a$ (mC cm <sup>-2</sup> )	$Q_c$ (mC cm <sup>-2</sup> )	$Q_c/Q_a$
TEA.3HF	Cu	0.10	-0.21	127.60	120.00	0.94
	Ag	0.15	0.14	Highly dissolving		
TEA.3HF/H <sub>2</sub> O (6%) (320 mV s <sup>-1</sup> )	Cu	0.45	-1.75	140.55	40.75	0.29
	Ag	-0.11	-0.75	1,536.51	338.03	0.20
TEA.3HF/AN (6%) (320 mV s <sup>-1</sup> )	Cu	-0.62	-0.50	759.53	251.54	0.33
	Ag	0.09	0.15	Highly dissolving		
TEA.3HF/PC (0.1 M)	Cu	-0.11	-0.62	67.61	46.32	0.60
	Ag	0.01	-0.04	416.60	65.22	0.16
TEA.3HF/Sulfolane (0.1 M)	Cu	-0.07	-0.79	37.84	20.08	0.53
	Ag	0.25	0.41	187.30	28.32	0.15

<sup>a</sup>  $E_{ia}$  and  $E_{ic}$  were measured at 2 mA cm<sup>-2</sup> for both Cu and Ag electrodes

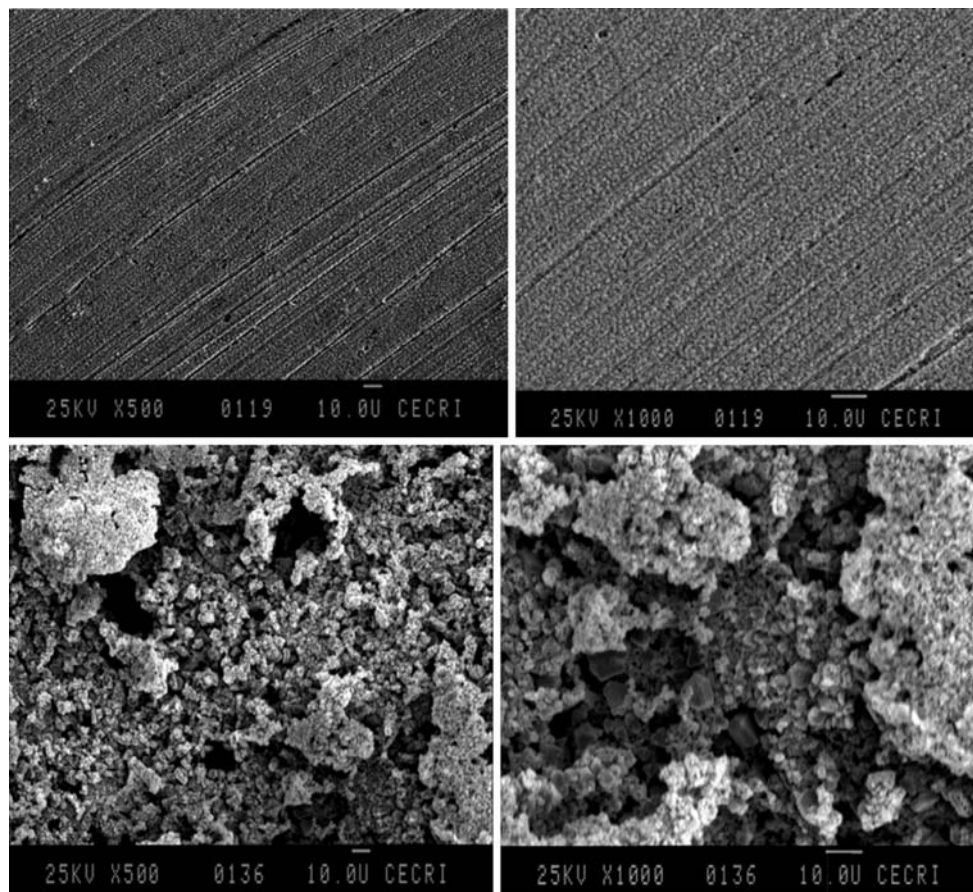
Ag electrodes were anodically polarized in neat TEA.3HF and 0.1 M of TEA.3HF/TBABF<sub>4</sub> containing different solvents (50 ml) at a slow sweep rate of 10 mV s<sup>-1</sup> within the corresponding potential limit (three cycles). After polarization, 0.1 ml of the electrolyte was pipetted out and made up to 10 ml using triple-distilled water, and this diluted portion was subjected for AAS analysis. Neat TEA.3HF as well as AN and PC containing 0.1 M TEA.3HF were soluble in water. However, due to poor solubility of sulfolane contain-

ing 0.1 M TEA.3HF, the electrolyte was initially extracted with water, and the extracted portion was diluted as described above and then analyzed.

## Results and discussion

In the present work, the anodic dissolution of Cu and Ag were firstly compared in solvent-free TEA.3HF ionic

**Fig. 2** SEM of **a, b** Cu and **c, d** Ag obtained after cyclic polarization in TEA.3HF at 40 mV s<sup>-1</sup>. Conditions are same as in Fig. 1. Magnifications **a, c** ×500, **b, d** ×1,000. Scale line corresponds to 10 μm



liquid. The influence of addition of a small weight percentage (6%) of water and acetonitrile in this medium on the voltammetric behavior was also studied (“Anodic behavior in TEA.3HF”). The influence of TEA.3HF and relatively more ionic supporting electrolyte such as TBABF<sub>4</sub> on the anodic behavior of Cu and Ag in non-aqueous solvents, namely, AN, propylene carbonate, and sulfolane, was investigated in “Anodic behavior in solvents containing 0.1 M TEA.3HF” and “Anodic behavior in solvents containing tetrabutylammonium tetrafluoroborate,” respectively. In “The influence of solvents and supporting electrolyte on the anodic dissolution—a comparative study,” a comparative study on the influence of solvents and supporting electrolytes on the anodic dissolution of the two electrodes are presented.

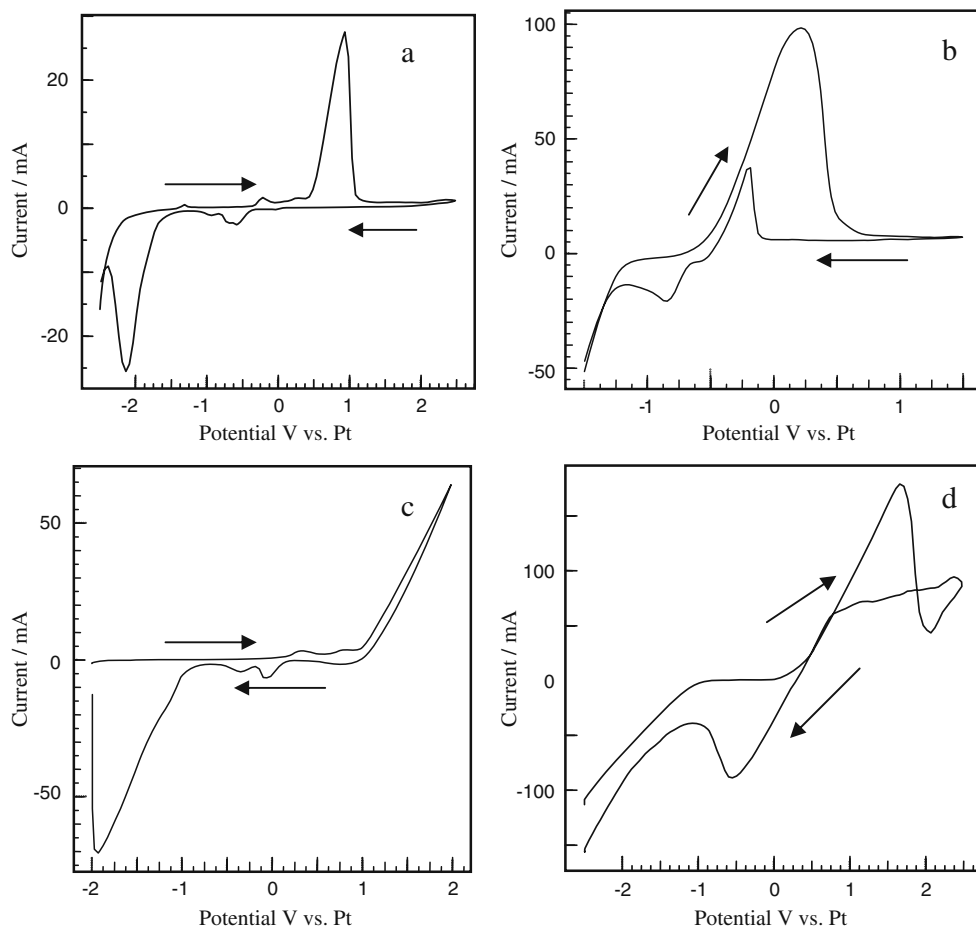
### Anodic behavior in TEA.3HF

Typical multisweep cyclic voltammograms of Cu and Ag at an identical sweep rate of 40 mV s<sup>-1</sup> are presented in Fig. 1a, b, respectively. Copper gives a well-defined anodic peak at around 0.1 V (A1) followed by two cathodic peaks at around -0.3 (C1) and -0.8 V (C2). For both systems, the

peak currents do not vary significantly during second and subsequent sweeps (Fig. 1a). On Ag electrode, the anodic and as well as cathodic dissolution currents are significantly higher than Cu, and they occur at widely different potential regimes (Fig. 1b). Apart from main anodic and cathodic peaks around 0.8 and -0.6 V, respectively, number of small anodic as well as cathodic peaks is observed during the polarization of Ag electrode in this medium. The anodic and cathodic currents also decrease significantly with increasing the cycle number (Fig. 1b).

Reversibility of redox process of any electrode material depends on the anodic and cathodic peak potentials as well as anodic and cathodic charges, obtained during the polarization studies. In the present work, however, no distinct anodic peaks appeared in the voltammograms of Cu and Ag electrodes during their polarization in most of the solvent-supporting electrolyte systems (see later). Hence, we have compared another pair of electrochemical parameters such as initial anodic potential,  $E_{ia}$  and initial cathodic potential  $E_{ic}$  of these two electrodes, instead of anodic and cathodic peak potentials in different electrolytes. From the respective voltammograms, both the  $E_{ia}$  and  $E_{ic}$  values are obtained by measuring the potential ( $V$ ) at a current density

**Fig. 3** Effect of addition of 6% of water (a, c) and AN (b, d) on the voltammetric behavior of Cu (a, b) and Ag (c, d), respectively. Sweep rate for Cu and Ag is 40 and 320 mV s<sup>-1</sup>, respectively

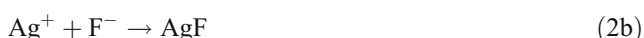


of  $2 \text{ mA cm}^{-2}$  (in some cases,  $1 \text{ mA cm}^{-2}$ ) in the anodic and cathodic sides, respectively.

The potential difference between  $E_{ia}$  and  $E_{ic}$  for Cu in TEA.3HF is around 0.11 V and indicates the reversibility of the anodic oxidation and cathodic reduction steps (Eqs. 1a and 1b)



and Ag (Eqs. 2a and 2b)



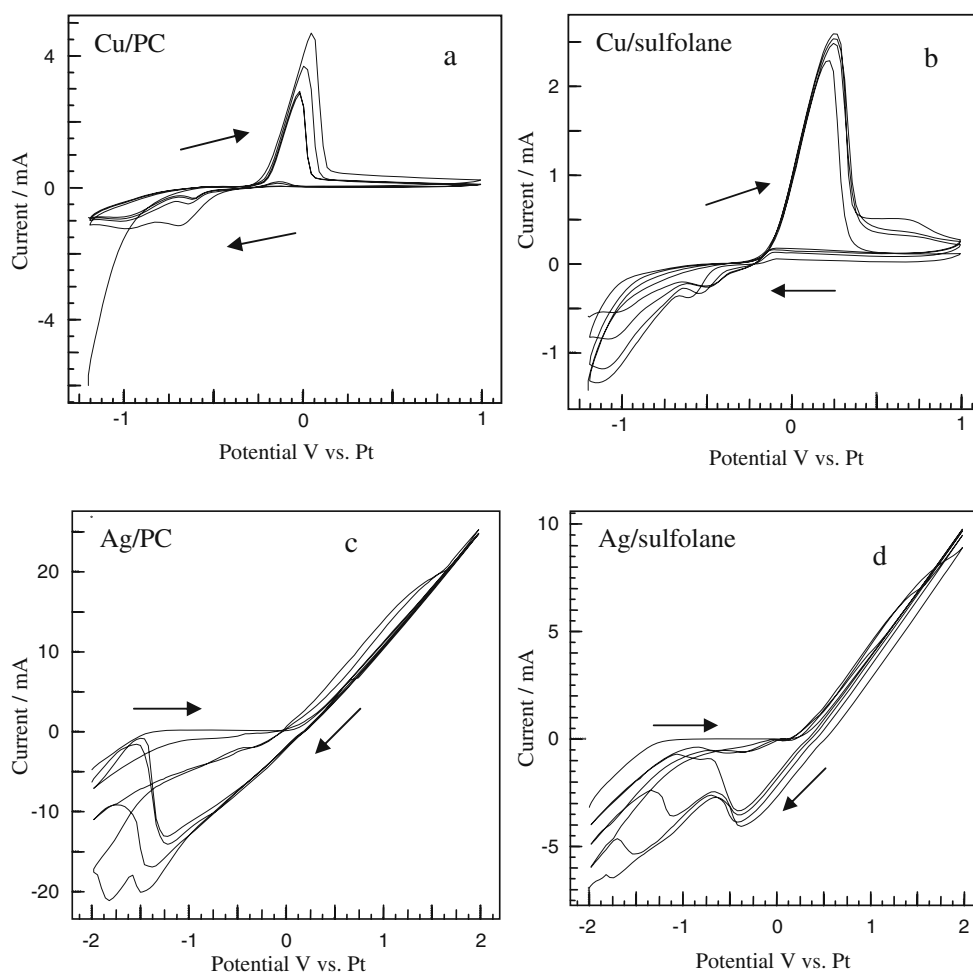
As indicated in Eqs. 1a, 1b, 2a, and 2b, both Cu and Ag undergo anodic dissolution (Eqs. 1a and 2a) and subsequent precipitation (Eqs. 1b and 2b)

The requirement for a well-defined reference electrode in non-aqueous fluoride media is the formation of a compact

fluoride film without significant dissolution of metal ions into the electrolyte solution. If we assume that only these metal ions as fluoride film present on the metal surface contributes towards the cathodic charge, the relative ratio of cathodic precipitation charge,  $Q_c$ , and the anodic dissolution charge,  $Q_a$ , relates to direct measure of film stability. Here,  $Q_a$  is the total anodic charge, which includes metal dissolution as well as insoluble surface fluoride film formation. However,  $Q_c$  is essentially a measure of reducible film present on the electrode surface, i.e., recoverable surface charge during potential cycling. These two parameters, along with  $E_{ia}$  and  $E_{ic}$  for both Cu and Ag in this medium, are summarized in Table 1.

In TEA.3HF,  $E_{ia}$  and  $E_{ic}$  values for Cu are indeed close, indicating reversible oxidation and reduction behavior (Table 1). The charge recovery ratio  $Q_c/Q_a$  is significantly high on Cu electrode, suggesting that in this medium, Cu can indeed serve as reference electrode. The Ag, however, undergoes substantial dissolution, and hence,  $Q_c$  and  $Q_a$  values are very high and significantly less reproducible. This phenomenon is also clearly reflected from SEM micrographs obtained after polarizing the Cu and Ag

**Fig. 4** Multisweep cyclic voltammograms of Cu (a, b) and Ag (c, d) in PC (a, c) and sulfolane (b, d) containing 0.1 M TEA.3HF at a sweep rate of  $40 \text{ mV s}^{-1}$ . Number of cycles=4



electrode under the multisweep polarization conditions represented in Fig. 1a, b, respectively. Very thin and smooth  $\text{CuF}_2$  films are observed on Cu electrode with small pores (Fig. 2a, b with two different magnifications). In contrast, Ag electrode exhibits a highly rough surface with large pores and deposited fluoride salts (Fig. 2a, b with two different magnifications).

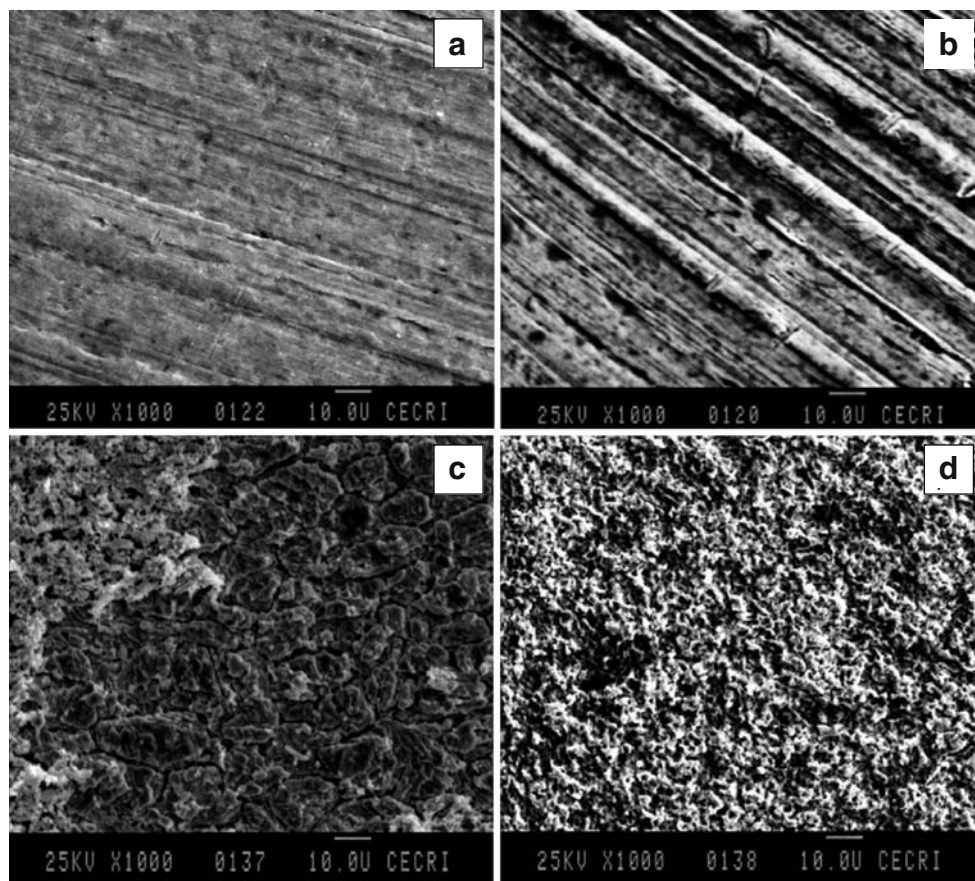
In TEA.3HF medium, addition of water and AN were found to influence the voltammetric behavior of Cu and Ag significantly (Fig. 3). In presence of water (6%), the main anodic oxidation process is initiated around 0.5 V and the main cathodic process by around  $-0.15$  V (Table 1, Fig. 3a). Many oxides, hydroxides, oxyfluorides, and hydroxy fluorides of Cu may be formed on the electrode surface with the addition of water, which can prevent anodic dissolution (very high  $E_{ia}$  value) and also influence the cathodic reduction of  $\text{CuF}_2$  (more negative  $E_{ic}$  value). In presence of the same percentage of AN,  $E_{ia}$  and  $E_{ic}$  values are found to be closer (Fig. 3b, Table 1). Acetonitrile enhances the solubility of  $\text{CuF}_2$  film. However,  $Q_a$  value is significantly high, indicating high anodic dissolution. The charge recovery ratio  $Q_c/Q_a$  value is found to be very low.

The voltammetric behavior of Ag in TEA.3HF containing water shows few similarities with that of Cu under identical experimental conditions. Since Ag electrode undergoes high dissolution and severe roughening in both TEA.3HF/water and TEA.3HF/AN during anodic polarization at slow sweep rates and the reproducibility itself becomes a major problem, the voltammograms were recorded at a very high sweep rate of  $320 \text{ mV s}^{-1}$ . The difference between  $E_{ia}$  and  $E_{ic}$  is found to be high (compare Fig. 3a, c). However, the dissolution proceeds without the formation of any distinct anodic peak (Table 1). Once again, in AN, Ag undergoes high dissolution, indicating more solubility of AgF film (Fig. 3d).

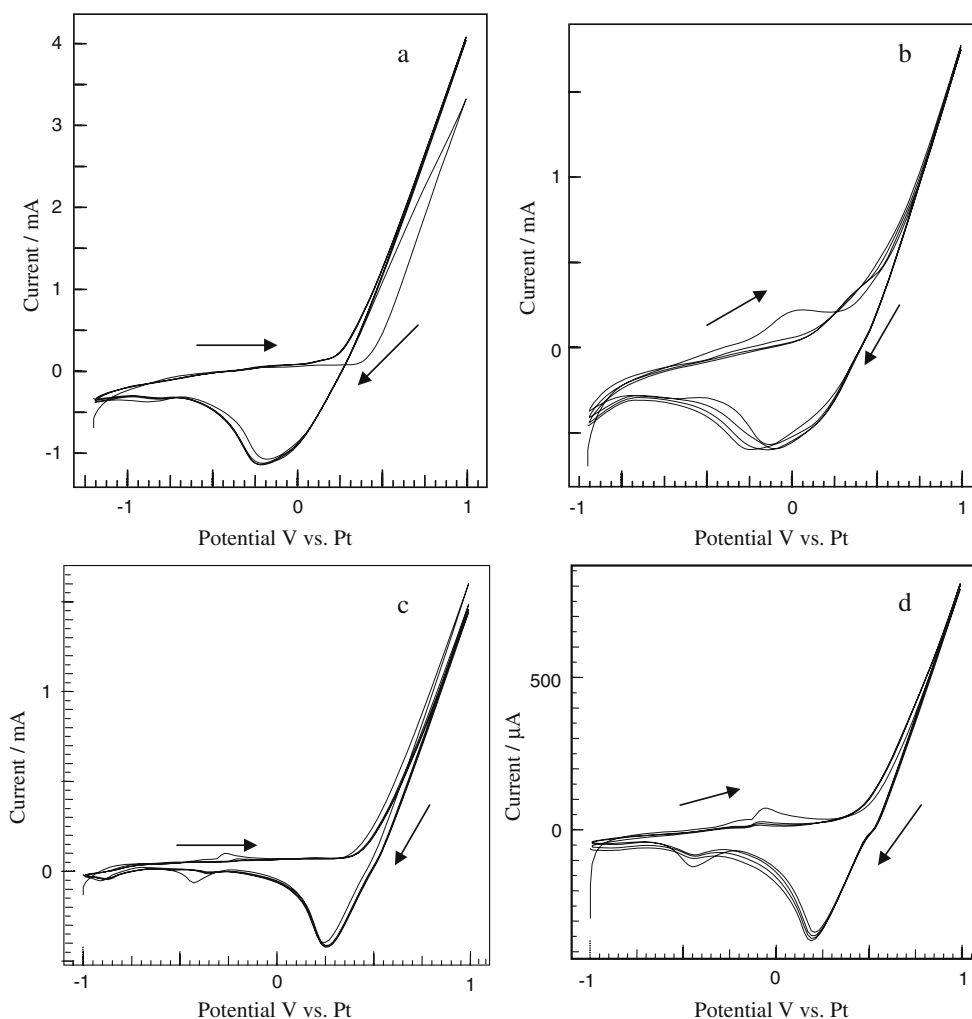
#### Anodic behavior in solvents containing 0.1 M TEA.3HF

Typical aprotic solvents, namely PC, sulfolane, and AN were considered for the present work. In AN containing 0.1 M TEA.3HF, Cu and Ag electrodes show high anodic dissolution, where getting reproducible voltammograms becomes a difficult task. However, in PC and sulfolane containing 0.1 M TEA.3HF, both the electrodes exhibit limited solubility of the fluoride films, resulting in

**Fig. 5** SEM of Cu (a, b) and Ag (c, d) obtained after cyclic polarization (four cycles) in PC (a, c) and sulfolane (b, d) containing 0.1 M TEA.3HF. Conditions are same as in Fig. 4. Magnifications (a–d)  $\times 1,000$ . Scale line corresponds to  $10 \mu\text{m}$



**Fig. 6** Multisweep cyclic voltammograms of Cu (a, b) and Ag (c, d) in PC (a, c) and sulfolane (b, d) containing 0.1 M TBABF<sub>4</sub> at a sweep rate of 40 mV s<sup>-1</sup>. Number of cycles=4



reproducible multisweep cyclic voltammetric responses. Hence, further voltammetric studies were done only in PC and sulfolane medium.

Typical multisweep cyclic voltammeteries (CVs) for Cu (Fig. 4a, b) and Ag (Fig. 4c, d) in PC (Fig. 4a, c) and sulfolane (Fig. 4b, d) containing 0.1 M TEA.3HF media, respectively, are shown here. The anodic peak potential remains the same in PC and slightly shifts towards anodic

side in sulfolane media. The anodic and cathodic currents decrease slightly with increasing the cycle number. There is no shift of cathodic peak potential in both the solvents. The difference between the  $E_{ia}$  and  $E_{ic}$  values was around 0.5 and 0.7 V and  $Q_c/Q_a$  by 0.6 and 0.5 for PC and sulfolane, respectively (Table 1).

No distinct anodic peak was observed in the multisweep voltammograms of Ag obtained in these solvents. The

**Table 2** Voltammetric characteristics of Cu and Ag electrodes in different solvents containing 0.1 M TBABF<sub>4</sub>

Electrolyte	Electrode	$E_{ia}$ (V) <sup>a</sup>	$E_{ic}$ (V) <sup>a</sup>	$Q_a$ (mC cm <sup>-2</sup> )	$Q_c$ (mC cm <sup>-2</sup> )	$Q_c/Q_a$
TBABF <sub>4</sub> /PC	Cu	0.44	-0.05	110.92	28.32	0.25
	Ag	0.71	0.25 <sup>b</sup>	51.88	18.19	0.34
TBABF <sub>4</sub> /sulfolane	Cu	0.80	-0.25 <sup>b</sup>	54.46	16.96	0.31
	Ag	0.82	0.21 <sup>b</sup>	34.33	17.97	0.52
TBABF <sub>4</sub> /AN	Cu	0.02	-0.03	329.41	28.94	0.09
	Ag	0.36	0.24	180.92	31.82	0.18

<sup>a</sup>  $E_{ia}$  and  $E_{ic}$  were measured at 2 mA cm<sup>-2</sup>

<sup>b</sup>  $E_{ia}$  and  $E_{ic}$  were measured at 1 mA cm<sup>-2</sup>

cathodic peaks were found to shift toward the negative direction, and the cathodic currents decrease significantly with subsequent cycles (Fig. 4c, d). Both the values of  $E_{ia}$  and  $E_{ic}$  are near to each other (Table 1). The  $Q_a$  value is very high, and  $Q_c/Q_a$  values are very low when compared to Cu (Table 1). The above results obtained during multisweep cycling of Cu and Ag in both these media was further confirmed by SEM investigations presented in Fig. 5. Copper electrode after cyclic polarization in PC (Fig. 5a) and sulfolane (Fig. 5b) in the anodic direction exhibits thin uniform porous layer on the polish lines of the electrode surface without the formation of any pits. On the other hand, the Ag electrode polarized in PC (Fig. 5c) and sulfolane (Fig. 5d), exhibits substantial roughness and porosity.

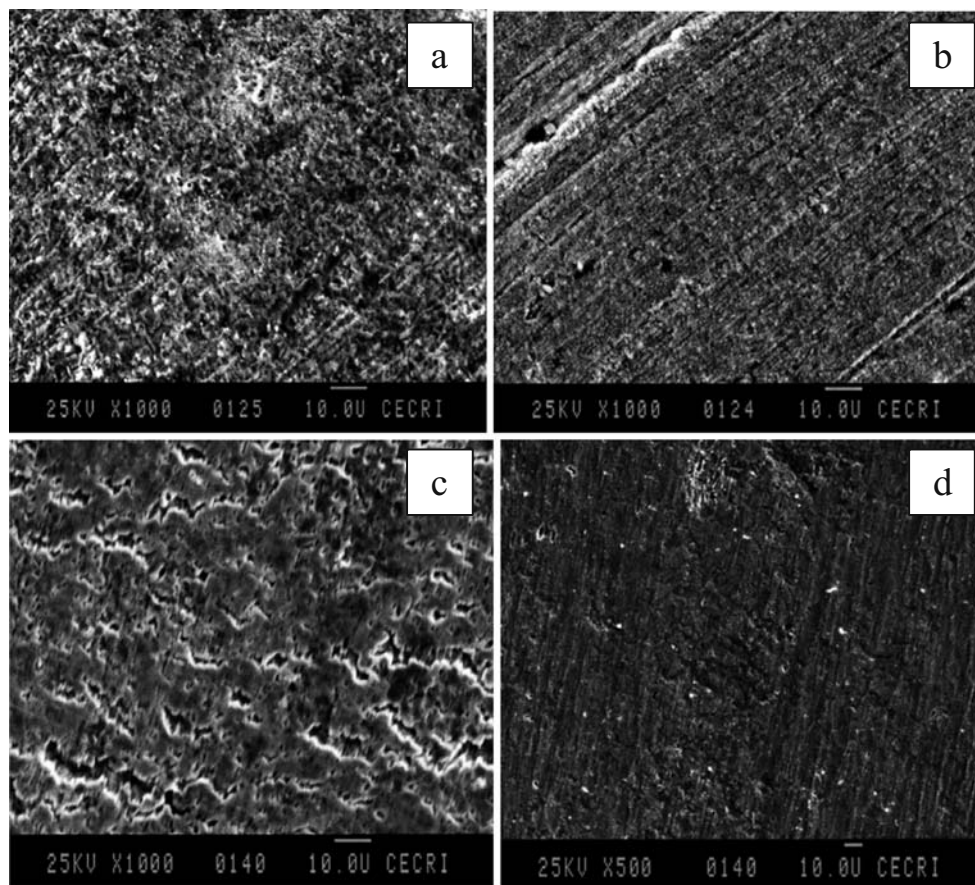
#### Anodic behavior in solvents containing tetrabutylammonium tetrafluoroborate

Anodic dissolution of Cu and Ag was also investigated in PC, AN, and sulfolane in presence of 0.1 M TBABF<sub>4</sub>, a more ionic supporting electrolyte. Quite interestingly, the reversal of dissolution rate between Cu and Ag is noticed in presence of solvents containing 0.1 M TBABF<sub>4</sub> when compared to TEA.3HF.

Typical multisweep voltammograms of Cu (Fig. 6a, b) and Ag (Fig. 6c, d) in PC (Fig. 6a, c) and sulfolane (Fig. 6b, d) in presence of 0.1 M TBABF<sub>4</sub> are shown here. No distinct anodic peaks were observed in the forward direction; however, the reverse scan follows one cathodic peak at around  $-0.2$  V for Cu and  $0.2$  V for Ag in both these solvents. The cathodic currents retrace with successive cycles. The  $E_{ia}$  and  $E_{ic}$  values were not close to each other (Table 2). However, the dissolution current for Cu were found to be always higher than the dissolution current for Ag. Quantitative data compiled in Table 2 also show high  $Q_a$  values and low  $Q_c/Q_a$  values for Cu. The SEM pictures obtained after the anodic polarization experiments for Cu (Fig. 7a, b) and Ag (Fig. 7c, d) also reflect the above observations. The anodic dissolution in sulfolane is generally lower than in PC for the two electrodes. However, the dissolution of Ag in this media is more uniform, and no significant pitting as well as surface roughening is noticed for Ag in presence of 0.1 M TBABF<sub>4</sub> (Fig. 7c, d) unlike that of 0.1 M TEA.3HF/solvents (Fig. 5c, d).

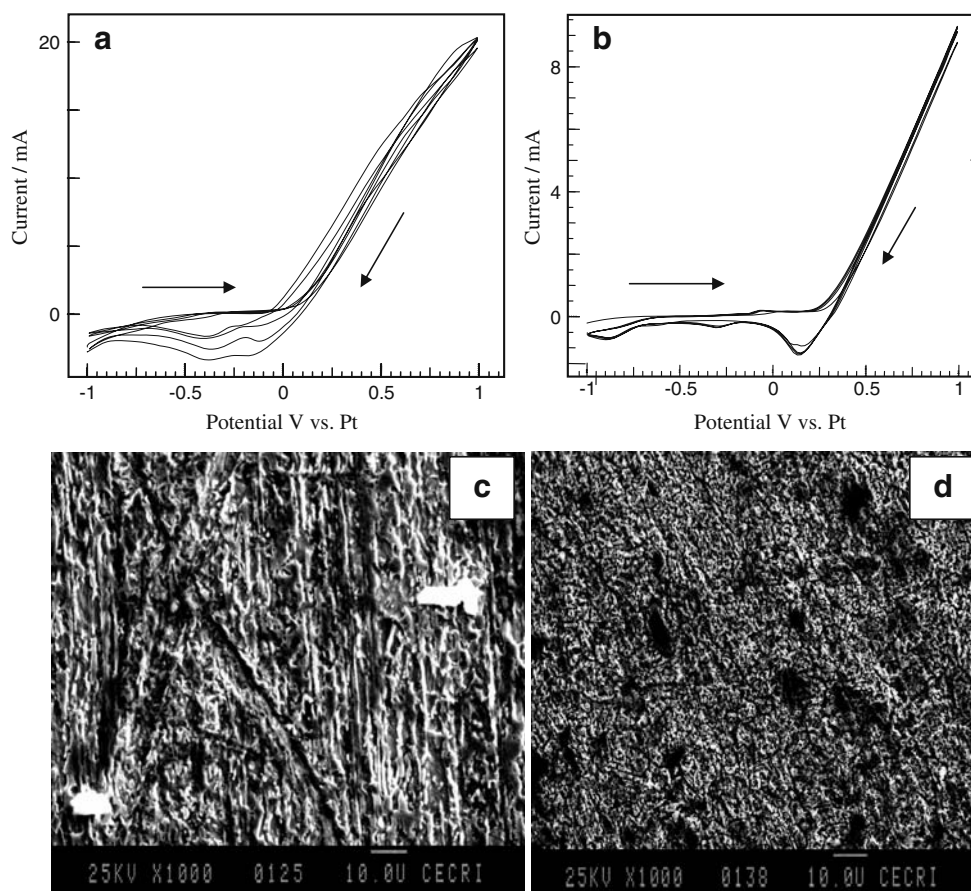
Even in AN, the anodic dissolution in presence of 0.1 M TBABF<sub>4</sub> could be investigated with good reproducibility. Typical multisweep CVs for Cu and Ag in AN containing 0.1 M TBABF<sub>4</sub> are shown in Fig. 8a, b. The voltammetric

**Fig. 7** SEM of Cu (a, b) and Ag (c, d) obtained after cyclic polarization (four cycles) in PC (a, c) and sulfolane (b, d) containing 0.1 M TBABF<sub>4</sub>. Conditions are same as in Fig. 6. Magnifications (a–c)  $\times 1,000$  and d  $\times 500$ . Scale line corresponds to 10  $\mu$ m





**Fig. 8** Multisweep cyclic voltammograms of **a** Cu and **b** Ag in AN containing 0.1 M TBABF<sub>4</sub> at 40 mV s<sup>-1</sup>. Number of cycles=4. **c, d** SEM micrographs of Cu obtained after cyclic polarization in the same medium at same sweep rate. Magnifications (**c, d** ×1,000)



responses are once again similar with responses obtained in PC and sulfolane containing TBABF<sub>4</sub> where there is no anodic peak evolution indicating the absence of any passive layer. The anodic dissolution charge on Cu is higher than that of Ag (Table 2). The SEM pictures also indicate substantial higher etching on Cu (Fig. 8c) when compared to Ag (Fig. 8d).

The influence of solvents and supporting electrolyte on the anodic dissolution—a comparative study

The  $Q_a$  and  $Q_c$  values for Cu and Ag in the five solvent-supporting electrolyte systems discussed so far are quantitatively compared in Fig. 9 (neat TEA.3HF is not included here for the comparison as both the cathodic and anodic charges for Ag are very high due to high dissolution). From the figure, it is noted that  $Q_a$  for Cu in PC (Fig. 9a) as well as sulfolane (Fig. 9b) are substantially lower than  $Q_a$  values for Ag in the above solvents containing 0.1 M TEA.3HF. An exactly opposite trend is noticed in solvent systems containing 0.1 M TBABF<sub>4</sub>, where  $Q_a$  values for Cu are greater in PC (Fig. 9c), sulfolane (Fig. 9d), and AN (Fig. 9e) than Ag. It appears that the supporting electrolyte rather than solvents play a significant role in deciding the anodic dissolution of the metals.

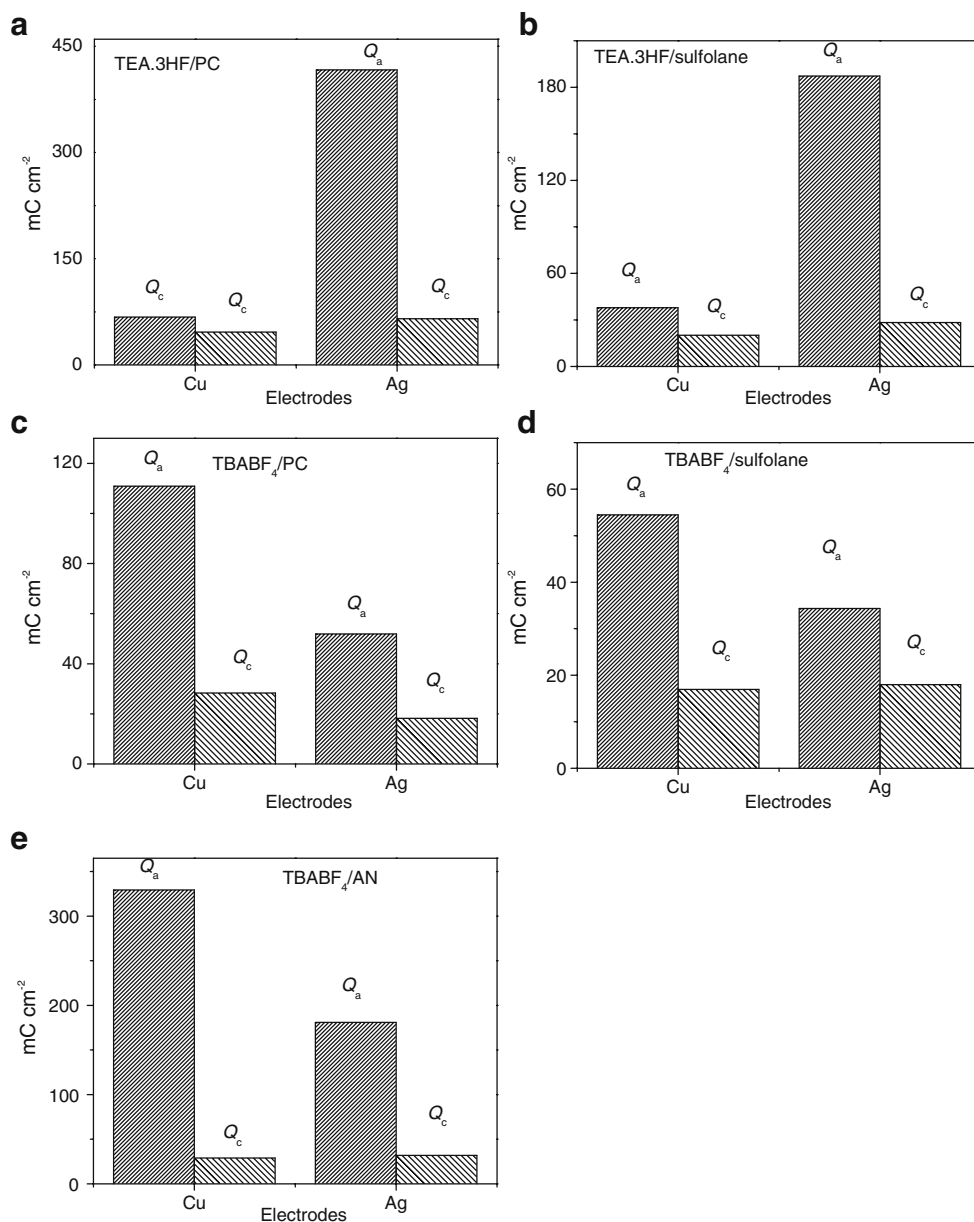
The anodic oxidation step for Cu (Eqs. 1a and 1b mentioned in “Anodic behavior in TEA.3HF”) depends on the relative stability of Cu<sup>2+</sup> and Ag<sup>+</sup> ions in the medium. In TEA.3HF medium, CuF<sub>2</sub> (Eq. 1b) and AgF appear to be the dissolution products. In TBABF<sub>4</sub> medium, precipitated products are Cu(BF<sub>4</sub>)<sub>2</sub> and AgBF<sub>4</sub>.



Based on the charge calculations in the aprotic solvent systems investigated here, it seems that AgF is more soluble than CuF<sub>2</sub>, whereas AgBF<sub>4</sub> is less soluble than Cu(BF<sub>4</sub>)<sub>2</sub>.

Further proof for the above conclusions on the anodic dissolution of Cu and Ag are obtained from AAS data for Cu<sup>2+</sup> and Ag<sup>+</sup> ions in the electrolyte systems under the same polarization conditions described in “Anodic behavior in solvents containing 0.1 M TEA.3HF” and “Anodic behavior in solvents containing tetrabutylammonium tetrafluoroborate.” The molar concentrations of Cu<sup>2+</sup> and Ag<sup>+</sup> ions obtained from different experiments are compared with the charge recovery ratios ( $Q_c/Q_a$ ) in Fig. 10a, b, respectively. Low  $Q_c/Q_a$  values correspond to high concentration

**Fig. 9** Effect of anodic and cathodic charge on the polarization of Cu and Ag in 0.1 M of **a** TEA.3HF/PC, **b** TEA.3HF/sulfolane, **c** TBABF<sub>4</sub>/PC, **d** TBABF<sub>4</sub>/sulfolane, and **e** TBABF<sub>4</sub>/AN



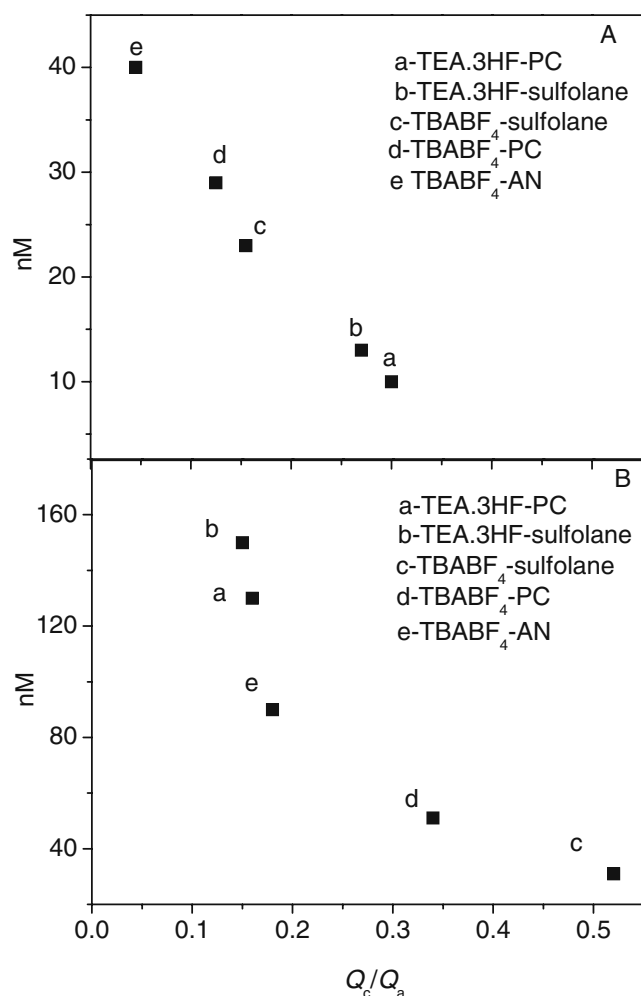
of metal ions in solution. From the figure, it is noted that Cu indicates the highest dissolution in AN (Fig. 10A, e) containing TBABF<sub>4</sub>. On the other hand, Ag shows maximum dissolution in PC (Fig. 10B, a) containing TEA.3HF. Further, the anodic dissolution of Cu and Ag in these three solvents decreases in the order AN > PC > sulfolane, irrespective of the presence of fluoride or fluoroborate ionic species, and this may be correlated with relative solubility of both these salts in these solvents as revealed by  $Q_a$  values as well as AAS data.

From the above studies, it is noted that the  $Q_a$  values are related to the relative solubility of Cu and Ag salts, while  $Q_c$  values are associated with the film thickness and its coverage on the electrode surface. In the present inves-

tigations, the  $Q_a$  values differ substantially between different solvents and supporting electrolytes. Typically for Cu and Ag,  $Q_a$  values vary between 330–38 and 416–34 mC cm<sup>-2</sup>, respectively. But, for both these metals,  $Q_c$  values fall within a short range of 65 to 17 mC cm<sup>-2</sup> which suggests that the surface coverage and film thickness of fluoride and fluoroborate salts of Cu as well as Ag lie only within this small range.

## Conclusions

The present work clearly indicates that the dissolution pattern and film formation behavior of Cu and Ag electro-



**Fig. 10** Plots of charge recovery ratio vs. metal fluoride (M) of **a** Cu and **b** Ag dissolved in different solvents containing 0.1 M TEA.3HF and TBABF<sub>4</sub>. The metal fluorides are formed by multisweep anodic polarization in the same electrolyte media for four cycles and are found out from the electrolyte solutions using AAS

des in neat TEA.3HF as well as AN, PC, and sulfolane containing 0.1 M TEA.3HF and TBABF<sub>4</sub> have many qualitative similarities, as noted from CV measurements, SEM morphology, and AAS analysis. In solvent-free TEA.3HF medium, the copper electrode shows high charge recovery ratio ( $Q_c/Q_a$ ), suggesting that in this medium, Cu

can certainly serve as reference electrode. However, on Ag electrode in the same medium, substantial dissolution produces roughened surface with large pores. Additives such as AN and water in TEA.3HF influence high anodic dissolution in both Cu and Ag electrodes.

The anodic dissolution and precipitation process for both Cu and Ag depends significantly on the nature of supporting electrolyte as well as solvents. Fluoride salts of Cu show lesser solubility than Ag, while fluoroborate salts shows the reverse trend in the investigated solvents. The AAS data suggest that, for a particular salt, which may be either fluoride or fluoroborate of Cu and Ag, the relative solubility decreases in the order AN > PC > sulfolane.

**Acknowledgments** The authors thank the Director, CECRI, Karaikudi for his keen encouragement in doing this work. The authors acknowledge the assistance of Ms. M. Deepa and Ms. A. Jasmine during the preliminary stage of this investigation.

## References

- Suriyanarayanan N, Noel M (2005) *J Appl Electrochem* 35:49
- Burrows B, Jasinski R (1968) *J Electrochem Soc* 115:348
- Germanz G, Nicolas F, Rouquette S, Lamirault S, Ferry D, Picard GS (1989) *Mater Sci Eng* 120–121:329
- Dumont H, Qian SY, Conway BE (1997) *J Appl Electrochem* 27:267
- Mimoto A, Miyazaki T, Yamashita J, Nagamine S, Inaba M, Tasaka A (2006) *J Electrochem Soc* 153:9
- Filliaudeau DJF, Picard GS (1993) *Electrochim Acta* 38:1951
- Dove MFA, Goodier M (1991) *J Fluorine Chem* 54:23
- Totir GG, Chottiner GS, Gross CL, Scherson DA (2002) *J Electroanal Chem* 532:151
- Noel M, Suriyanarayanan N, Suryanarayanan V (2001) *J Solid State Electrochem* 5:419
- Devynck J, Fabre PL, Tremillion B, Benhadid A (1978) *J Electroanal Chem* 91:93
- Gatner K, Zieba A (1995) *Polish J Chem* 69:1315
- Sneddon DD, Gewirth AA (1995) *Surf Sci* 343:185
- Zhang SS (2006) *J Power sources* 162:1379
- Zhang SS, Xu K, Jow TT (2006) *J Power sources* 156:629
- Noel M, Suryanarayanan V, Chellammal S (1997) *J Fluorine Chem* 83:31
- Fuchigami T, Higashiya S, Hou Y, Dawood KM (1999) *Rev Heteroatom Chem* 19:67