

DEPENDENCE OF Ag-SOLVENT INTERACTIONS ON THE CRYSTALLOGRAPHIC ORIENTATION OF THE METAL SURFACE

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In previous work [1] we have shown that ionic and non-ionic adsorption on Ag single crystal face electrodes is strongly dependent on nature and strength of metal-water interactions, since water molecules are replaced at the interface by the adsorbing species. Metal water interactions have been found to be face specific, the sequence being (111) < (100) < (110). However, strongly adsorbed species conceal the effect of water desorption since metal-adsorbate interactions prevail, while water desorption dominates clearly in the case of weakly adsorbed species, although differences between the various faces are soothed down.

In this work we have investigated Ag-water interactions using three indirect experimental approaches: (a) Adsorption of weakly adsorbed neutral organic species at the potential of maximum adsorption; (b) Substitution of electrolyte solutions in aprotic solvents for aqueous electrolyte solutions; (c) Adsorption of water from non-aqueous electrolyte solutions and study of oxide formation on single crystal and polycrystalline faces of Ag.

Experiments were carried out with Ag single crystals prepared, oriented and polished following the procedure described in a previous work [2]. Adsorption of acetonitrile (ACN) was studied by impedance measurements in KClO₄ aqueous solutions at constant frequency and slow potential scan rate (shown in Fig.1)

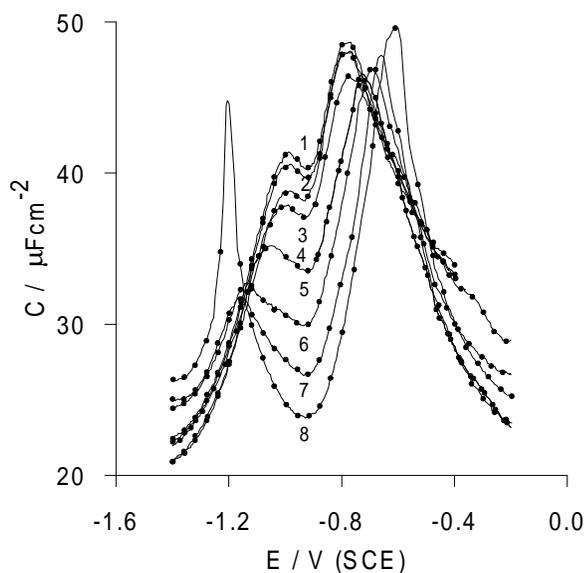


Fig.1 Capacitance/potential curves at 10 mVs⁻¹ of Ag(100) in 0.1 mol dm⁻³ KClO₄ aqueous solution and various concentrations of ACN from 0.035 to 1.84 mol dm⁻³.

and at constant potential in the double layer region during sweep of frequencies from 10 Hz to 1000 Hz

The technique of surface preparation, the careful cleaning of solutions from impurities and oxygen, as well as the automatic registration of the experimental data has allowed the time of experiments to be considerably reduced. The studies in KPF₆ and NaClO₄ solutions in ACN were mainly performed by means of cyclic voltammetry (Fig.2).

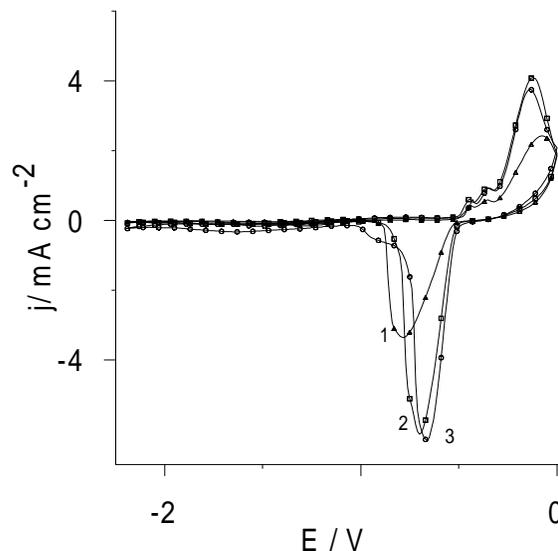


Fig.2 Potentiodynamic j/E curves at 100 mV s⁻¹ of Ag in 0.1 mol dm⁻³ KPF₆ in ACN solutions: 1) (110); 2) (100); 3) - (111).

The parameters of ACN adsorption will be compared with literature data for different electrodes in aqueous solutions. The influence of water in ACN on the anodic formation of silver oxide will be discussed in the light of previous results in purely aqueous solution [3]. The amount of water in ACN was changed from 0.05 to 7 mol dm⁻³.

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References

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