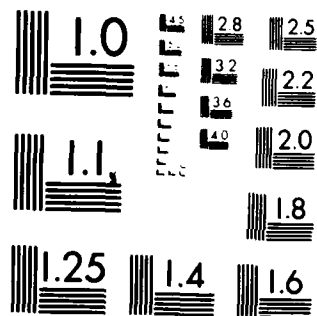


AD-A133 202 POLYMER COATED ELECTRODES IN AMBIENT TEMPERATURE MOLTEN 1/1
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CHEMISTRY P G PICKUP ET AL. 01 AUG 83 SUNYBUF/DC/TR-14
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ambient temperature molten salts, specifically the N-n-butylpyridinium chloride-aluminum chloride system, have been shown to be useful solvents for studying polymer films on solid electrodes. The electrochemical behavior of $[Ru(2,2'-bipyridine)_2(4-vinylpyridine)_2]^{2+}$, polyvinylferrocene and thionine polymers have been investigated in basic, neutral and acidic melts. Behavior is similar to that reported for these polymer films in other non-aqueous solvents, such as acetonitrile, or water, and may be somewhat enhanced.		

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TECHNICAL REPORT NO. 14

POLYMER COATED ELECTRODES IN
AMBIENT TEMPERATURE MOLTEN SALTS

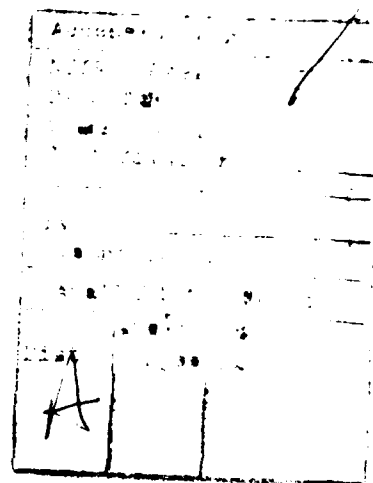
by

P.G. PICKUP AND ROBERT OSTERYOUNG

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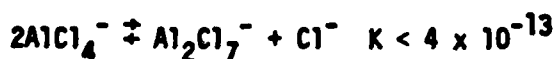
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We were interested in investigating redox polymer films on solid electrodes (1) in a molten salt. We have therefore investigated the electrochemistry of poly-[Ru(2,2'-bipyridine)₂(4-vinylpyridine)₂]²⁺ (2), polyvinylferrocene (PVF) (3,4) and thionine polymer (5) coated glassy carbon electrodes in various compositions of the ambient temperature molten salt system aluminum chloride:n-butylpyridinium chloride (BuPyCl) (6) at 40°C. Electrodes were coated with polymer as described in references 2, 4, and 5 respectively. Surface coverages were measured by cyclic voltammetry in 0.1 M Et₄NClO₄/CH₃CN for the ruthenium and PVF polymers and in 0.05 M aqueous H₂SO₄ for the thionine polymer.

We have used the 0.95:1 (basic), 1:1 (neutral) and 1.2:1 (acidic) AlCl₃:BuPyCl mole ratio melts in which the dominant equilibrium is (7):



The "neutral" melt can be described as BuPy⁺AlCl₄⁻. The basic melt may be considered to consist of BuPy⁺, Cl⁻ and AlCl₄⁻ ions and the acidic of BuPy⁺, Al₂Cl₇⁻ and AlCl₄⁻, the content depending on the stoichiometric ratio of AlCl₃ to BuPyCl. Potentials are quoted relative to Al in a 2:1 melt, which is ca. +140 mV relative to SCE in CH₃CN (8).

The cyclic voltammetry of a C/poly-[Ru(bpy)₂(vpy)₂]²⁺ electrode in an acidic melt (Figure 1) was almost featureless on the first scan. Additionally, no electrochemistry of dissolved ferricenium (E⁰ = 0.24 V) was observed. On subsequent scans a well defined, reversible wave developed at E⁰ = +1.26 V and after this wave had reached ca. 80% of its final size a small membrane diffusion type wave (9) for ferricenium reduction developed at ca. +0.3 V. The voltammogram of Figure 1 reached steady state after about 40 scans and the final charge

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Key Words: Fused salts, electrode, voltammetry

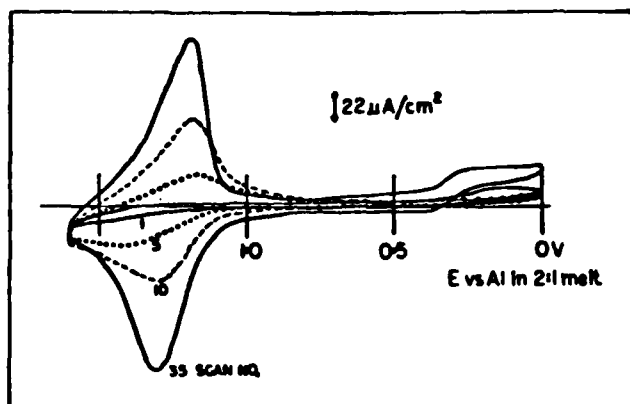


Figure 1. Cyclic voltammograms at 40°C of a C/poly-[Ru(bpy)₂(vpy)₂]²⁺ electrode (surface coverage = 2.0×10^{-9} mol/cm²) in 1.2:1 AlCl₃:BuPyCl melt containing ferricenium (ca. 1 mM). Scan speed = 100 mV/s.

under the wave at +1.26 V corresponded to 100% of the polymer originally present. Thicker films require a longer break-in period.

We interpret the above behavior as indicating slow permeation of melt and ferricenium ions into the polymer film. This permeation is facilitated by repeated oxidation and reduction of the polymer since it does not occur when the polymer is maintained in its reduced state and it is very slow when the polymer is exhaustively oxidized. Presumably the counter-ion and polymer backbone movements associated with oxidation and reduction of the polymer (4,10) allow melt to diffuse into the polymer. This interpretation is supported by the gradual appearance of chloride (from AlCl₄⁻ or Al₂Cl₇⁻) oxidation and Al deposition at the limiting potentials of the acidic melt if the potential is scanned through the normal electrochemical window of the melt (6) during break-in. Once an electrode has been broken in it remains electroactive for extended periods (days) in the melt. This type of break-in behavior has been observed by other workers, using different polymers and more conventional solvents (water (4) and acetonitrile (10)).

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Once a ruthenium polymer film has been broken in, it exhibits well defined electrochemistry in both neutral and acidic melts (the basic melt is more easily oxidized than the polymer). For films of 3×10^{-9} mol/cm² or less, reversible electrochemistry is observed at scan speeds as high as 500 mV/s. Peak separations are constant and peak currents vary linearly with scan speed, characteristic of a surface bound redox couple. Thicker films show evidence of slow charge transport at scan speeds above 100 mV/s, with increasing peak separation and decreasing charge as the scan speed is increased. The formal potential of the polymer in the melt is about 100 mV greater than expected in comparison to ferrocene/ferrocenium, the respective redox potentials of these couples being 1.22 V and 0.38 V vs SCE in acetonitrile.

To obtain a well defined voltammogram of a drop coated C/polyvinylferrocene electrode required that it first be cycled through the PVF redox wave in neutral or basic melt (the polymer dissolves in acidic melt) and then in acetonitrile/Et₄NClO₄. After washing with acetone to remove Et₄NClO₄ from the polymer and drying in the vacuum port of the dry-box the electrode shows well defined electrochemistry in the melt after a break-in period similar to that observed for the ruthenium polymer. Generally, the final voltammogram (Figure 2) shows stable, reversible electrochemistry at E° ≈ 0.25 V. However, the quantity of polymer as deduced from the charge is always significantly less than was originally deposited onto the electrode, usually corresponding to 5-20 monolayers of monomer units.

Thionine polymer also exhibits a break-in period in the melt. Final voltammograms (Figure 3) show quasi-reversible electrochemistry at E° ≈ 0.25 V with the peak separation increasing with scan speed. However, the voltammograms in the melt compare well with those obtained in aqueous sulphuric acid (5).

The results presented here indicate that three very different redox polymer coated electrodes function well in these anhydrous, highly conducting ambient temperature ionic liquids and we feel there is great potential for the use of such electrodes in such media. Other ambient temperature ionic liquids, such as the dialkylimidazolium chloroaluminates (11) would also appear to be useful for studies of polymeric electrodes. The use of such liquids for studies of electronically conducting polymers such as polyacetylenes, polypyrroles and others also appears to have considerable scientific and perhaps technological significance. Smyrl and co-workers

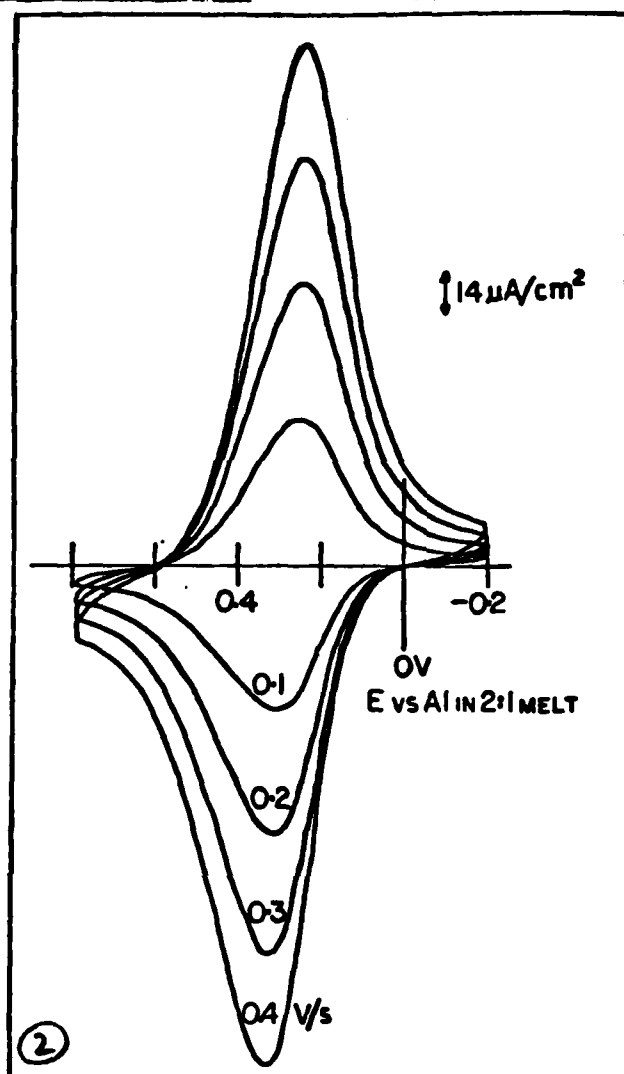


Figure 2. Cyclic voltammograms at 40°C of a C/polyvinylferrocene electrode (final surface coverage = 1.3×10^{-9} mol/cm²) in 0.95:1 AlCl₃: BuPyCl melt.

recently reported on impedance studies at polyacetylene coated electrodes in a 2:1 AlCl₃:BuPyCl melt (12); in this melt composition only the oxidation of the polyacetylene could be observed since the melt "window" is ≈ 2 V. However, use of a "neutral" system, either the butylpyridinium chloride or dialkylimidazolium chloride - aluminum chloride ionic liquid, might render such conducting polymers susceptible to both oxidation and reduction, since solvent limits of ca. 3.5 and 4.5 V, respectively, are observed (13). There are possible applications of polymer coated electrodes in these molten salt systems in the fields of electrocatalysis, fuel cells, photoelectrochemistry and batteries. Additional studies in this area are in progress in our laboratory.

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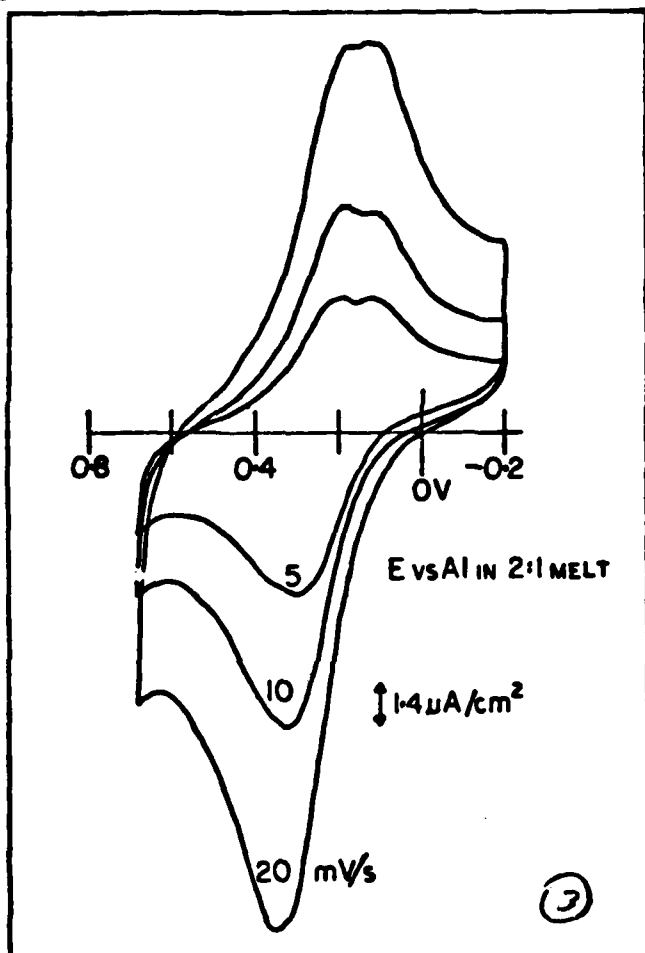


Figure 3. Cyclic voltammograms at 40°C of a C/thionine polymer electrode (surface coverage = 1.9×10^{-9} mol/cm²) in 0.95:1 AlCl₃:BuPyCl melt.

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