

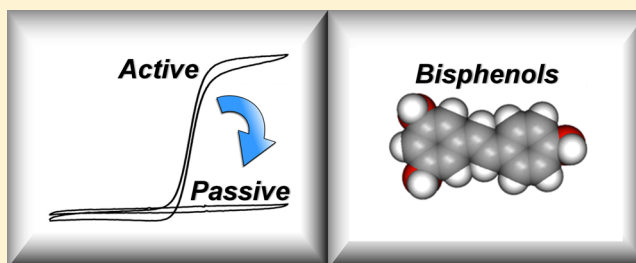


Poly(bisphenol) Polymers as Passivating Agents for Carbon Electrodes in Ionic Liquids

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ABSTRACT: Poly(bisphenol) polymers are identified as a new class of passivating agents for carbon electrodes in ionic liquids. They are inert and can readily be deposited as thin, conformal films by electropolymerization. Unlike conventional poly(monophenol) polymers, a single voltammetric scan is sufficient to accomplish their deposition. This is seen, for example, in the cases of poly(bisphenol A) and poly(bisphenol P). In each case, the thickness of the electropolymerized films is determined by the quantum tunneling distance of the faradaic electrons. Thus, film growth terminates when the faradaic electrons can no longer transit the film at a measurable rate. At that point, all the faradaic reactions cease, while the capacitive charging processes continue unabated. Experimentally, film thicknesses are observed in the range 4–30 nm. A challenging test for the poly(bisphenol) polymers is to coat them onto arrays of microelectrodes (RAM electrodes). Normally, microelectrodes are difficult to coat by electropolymerization due to the intense flux of soluble intermediates away from their surfaces. In the present work, however, coating is facile due to the extreme insolubility of the intermediates. This same property makes the films strongly adherent. Such remarkable behavior suggests that poly(bisphenol) films may have an important role to play as passivating agents in supercapacitors. They may also find application in other areas of technology that require thin-film passivity, such as nanostructural engineering and device physics.



INTRODUCTION

The corrosion of condensed phase matter continues to impede the progress of humanity. In particular, the destruction of the surface functionality of many modern technologies by chemical reaction with the environment is a significant drain on the world's economy. In the US alone, it has been estimated that the annual cost of surface corrosion exceeds 3% of the nation's gross domestic product,¹ corresponding to \$520 billion in 2014.² That is equal to one-seventh of the federal budget. In the vast majority of cases, corrosion occurs because of the electrochemical instability of a solid phase in the presence of a liquid phase. The result is a gradual (sometimes catastrophic) degradation of the functionality of solid surfaces.

The traditional countermeasure to corrosion is passivation. Passivation is the formation of an intermediate phase between the solid surface and the liquid environment, which causes the rate of corrosion to be significantly diminished. The intermediate phase may form spontaneously (as in the case of tarnish or rust) or it may be engineered deliberately. In either case, the hoped-for outcome is the formation of a semiconducting phase having a low concentration of electronic states in its bandgap. Such a phase is desirable because it inhibits the rate of corrosion even when the driving force is large.^{3–5}

All passivated systems are thermodynamically unstable. To gain insight into their breakdown mechanisms, many accelerated life tests have been performed over the past 50 years, typically involving extremes of voltage, temperature, and mechanical load.⁶ As a result of these tests, four principal failure

modes have been identified, namely (i) surface dissolution, (ii) high-field migration of anions and cations, (iii) electron and hole tunneling, and (iv) dielectric breakdown. To suppress them all, it is now generally accepted that passive films should be insoluble ($K_{sp} < 10^{-10} \text{ M}^2$), devoid of mobile ions ($< 10^{-7} \text{ M}$), depleted of localized states ($< 10^{19} \text{ cm}^{-3}$), and possessed of a wide bandgap ($> 3 \text{ eV}$). Perhaps unsurprisingly, these are exactly the same characteristics as those required of good insulators in high-voltage dc transmission.⁷

In the present work, we describe the use of an electrochemical technique (electropolymerization) to screen candidate polymers for the passivation of carbon surfaces in hydrophobic ionic liquids. Our purpose is to identify surface-protecting films for next-generation supercapacitors.⁸ In order to achieve this goal, it is necessary for the polymer films (of thickness d , say) to be thin enough to maintain electrode capacitance but thick enough to “switch off” the tunneling of electrons and holes into redox species in solution ($2 < d < 30 \text{ nm}$).

The energy E stored in a carbon-based supercapacitor is given by the relation

$$E = \frac{1}{2} CV^2 \quad (1)$$

where C is the capacitance of the device and V is the cell voltage. Maximization of stored energy requires the max-

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imization of V , which in turn requires the use of a nonaqueous solvent such as an ionic liquid. To prevent the ingress of water, it is also helpful if the solvent is hydrophobic. For this combination of reasons, considerable interest attaches to “designer” ionic liquids having wide voltage windows and perfluorinated anions,⁹ such as butyltrimethylammonium bis(trifluoromethylsulfonyl)imide (BTM-TFSI). Given the high voltages that are sought, considerable interest also attaches to the formation of passivating films that can extend the life of the electrodes.

For supercapacitors, candidate polymers of the poly(phenol) type are particularly interesting because of their low chemical reactivity and high electrical resistance.¹⁰ As noted by Crooks et al.,¹¹ these compounds open up the possibility of nano-engineering carbon surfaces. When formed by free-radical polymerization, poly(phenol) polymers also tend to cross-link spontaneously, rendering them insoluble in common solvents.

Historically, most research on poly(phenol) films has focused on wastewater treatment^{12–19} and metal protection.^{20–29} In the case of wastewater treatment, the poly(phenol) films are problematic, since they block the surfaces of catalysts. In the case of metal protection, however, the poly(phenol) films are beneficial, as they help prevent the corrosion of surfaces.

Although it is possible to form insoluble poly(phenol) polymers directly, without a dedicated cross-linking step, many research groups have opted to use one anyway. In a celebrated example, due to Mengoli et al.,³⁰ phenol was electropolymerized in a water/methanol/2-ethoxyethanol mixture and then cross-linked using allylamine. This method was later adopted by many other workers, such as Potje-Kamloth et al.,³¹ Kawagoe et al.,³² and El-Giar et al.³³ The only problem with the method is that it generates thick films (ca. 20 μm). For supercapacitors, it would be preferable to have much thinner films (ca. 20 nm) which do not damage the electrode capacitance. That is the target of the present work.

EXPERIMENTAL SECTION

Equipment and Instrumentation. Voltammetry experiments were carried out using an AutoLab PGSTAT 20 or a μ -Autolab 70282 (type II) potentiostat (Metrohm-Autolab, Eco-Chemie, Utrecht, The Netherlands). The operating software was General Purpose Electrochemical System (GPES), version 4.9 (Eco-Chemie Utrecht, The Netherlands). No IR compensation or noise filters were applied. High temperature conductivity and voltammetry experiments were carried out using a F25-ME thermostatic oil bath with external circulation (Julabo Labortechnik GmbH, Seelbach, Germany). The operating software was EasyTemp, version 3.20, (Julabo Labortechnik GmbH, Seelbach, Germany). Counter electrodes were made in-house. A 4 cm^2 platinum gauze mesh (Aldrich, 99.9%, 52 mesh, CAS: 7440-06-4) was spot-welded onto platinum wire. The platinum was flame-annealed before use. Saturated calomel electrodes were used in aqueous solutions. Liquid junctions with cell solutions were made inside porous glass disks. A silver–silver chloride (Ag|AgCl) pseudoreference electrode was used in all ionic liquids. The principal working electrode was a glassy carbon (GC) disk electrode ($r = 1.5$ mm, Bioanalytical Systems Inc., Warwickshire, UK). A random assembly of carbon microdisks (RAM electrode) was also used (Figure 1). For high temperature electrochemistry ($T > 25$ °C), a glassy carbon disk in a glass-filled Teflon shroud was used ($r = 1.5$ mm, Metrohm, Herisau, Switzerland). RAM electrodes (CSIRO, Melbourne, Australia) consisted of ca. 800 carbon

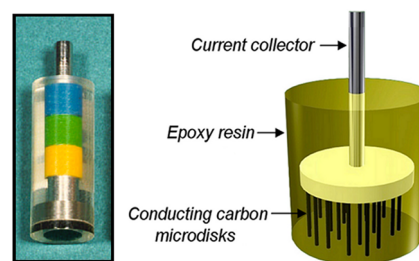


Figure 1. Photograph of a RAM electrode (left) and a conceptual schematic (right).

microdisks ($r = 3.5$ μm) distributed randomly within 1 cm^2 of working surface, set in a cured epoxy resin. According to Fletcher and Horne,³⁴ the number of microdisks that are active in a given experiment can be estimated by dividing the observed limiting current for the reduction of 1.0 mM potassium ferricyanide (aqueous) by 1.05 nA.

Electrode Preparation. Electrodes were polished using 0.3 μm alumina powder (Alpha Alumina Powder, Kemet, Greenville, USA) and a Buehler polishing cloth (Microcloth, Buehler, Coventry, UK) for at least 30 s. The electrodes were then washed in a 50/50 mixture of water and concentrated nitric acid to remove adventitious adsorbates and then sonicated in triply distilled water. Nonpolishable platinum electrodes (wires, sheets and meshes) were flame treated ($T > 500$ °C) and washed in concentrated nitric acid followed by triply distilled water. MarvinSketch, version 5.3 (2010), was used for drawing 2D chemical structures, and MarvinSpace, version 5.3 (2010), was used for modeling chemical structures in 3D. Jasc Paint Shop Pro, version 7, was used for image formatting. Analysis of data was carried out using Microsoft Office Excel (2010). Graphs were plotted using OriginLab, version 6.1 (2001). All ionic liquids were custom synthesized by Iolitec (Ionic Liquid Technologies, GmbH, Heilbronn, Germany). They were dried at 130 °C ($t > 1$ h) prior to use, and their purity was confirmed by carbon-13 nuclear magnetic resonance spectroscopy. Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide (BTM-TFSI) was the principal ionic liquid used.³⁵

All lab reagents were purchased from Fisher-Scientific (Loughborough, UK). Resveratrol (CAS: 501-36-0); bisphenol A (CAS: 1478-61-1); 4,4'-(hexafluoroisopropylidene)diphenol (CAS: 1478-61-1); 4,4'-(1,4-phenylenediisopropylidene)bisphenol; and 4,4'-sulfonyl-diphenol (CAS: 80-09-1) were purchased from Sigma-Aldrich, (Dorset, UK). All water was obtained from a Millipore Milli-Q gradient A10 water system (18.2 M Ω internal standard) and was triply filtered. Nitrogen gas was supplied in a BOC cylinder (The Linde Group, UK) and passed through a silica drying trap prior to use.

RESULTS

Faradaic Reactions. Faradaic reactions are electron transfer reactions that occur at the electrode–solution interface. In general, faradaic reactions may be either reversible or irreversible. Inside supercapacitors, reversible reactions simply add into the classical capacitance and are therefore harmless, but irreversible reactions tend to cause material degradation. Accordingly, there is a need to block irreversible faradaic reactions. A notorious problem is that even if the main components of the electrolyte solution are inert, irreversible faradaic reactions may still occur as a result of impurities or as a result of solvent decomposition.

Passivation of Faradaic Reactions. It is well-known that electron transfer takes place at electrode surfaces by a process of quantum tunneling from an occupied orbital near the Fermi energy of the electrode into an unoccupied orbital of the reactant molecule (or vice versa).³⁶

In the simplest case—that of short-range orbital overlap—the probability of electron tunneling depends on the square of the overlap integral, S_{DA} . Empirically, this parameter is found to decrease exponentially with distance between the donor and acceptor, eq 2, where x is the internuclear distance, and A and C are system constants:

$$S_{DA} \approx A \exp(-Cx) \quad (2)$$

As a result, inorganic insulators as thin as 2 nm can passivate electrode surfaces. The classic example is amorphous silicon dioxide (SiO_2), which is used as a gate material in MOSFETS (metal oxide semiconductor field-effect transistors). For polymeric insulators, however, somewhat thicker films are needed to achieve passivation due to the presence of localized states. These support long-range tunneling phenomena (such as superexchange³⁷ and hopping³⁸) in addition to the classic short-range tunneling mechanism.^{39,40} Consequently, polymeric insulators must generally be >2 nm thick to prevent electrons from leaking through. This was confirmed in the present work, where we found that the electrodeposition of most phenol-based polymers did not become self-limiting until $d > 4$ nm.

For the case of electron transfer by direct orbital overlap, the rate constant for electron transfer is related to the overlap integral by the expression³⁶

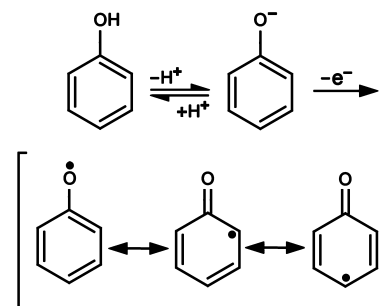
$$k_{\text{et}} = \frac{2\pi}{\hbar} |H'|^2 S_{DA}^2 \frac{N_A}{\sqrt{4\pi\lambda_m RT}} \exp\left(\frac{-(\lambda_m + \Delta G_m^0 + FE_F)^2}{4\lambda_m RT}\right) \quad (3)$$

where k_{et} is the rate constant for electron transfer, \hbar is the reduced Planck constant, H' is a constant, S_{DA} is the overlap integral, N_A is the Avogadro constant, λ_m is the reorganization energy per mole, ΔG_m^0 is the difference in molar Gibbs energy between the acceptor and the product, and E_F is the Fermi energy of the electrons inside the electrode. Inspection of eq 3 reveals that it is the decay of orbital overlap that limits the tunneling distance to about 2.0 nm.

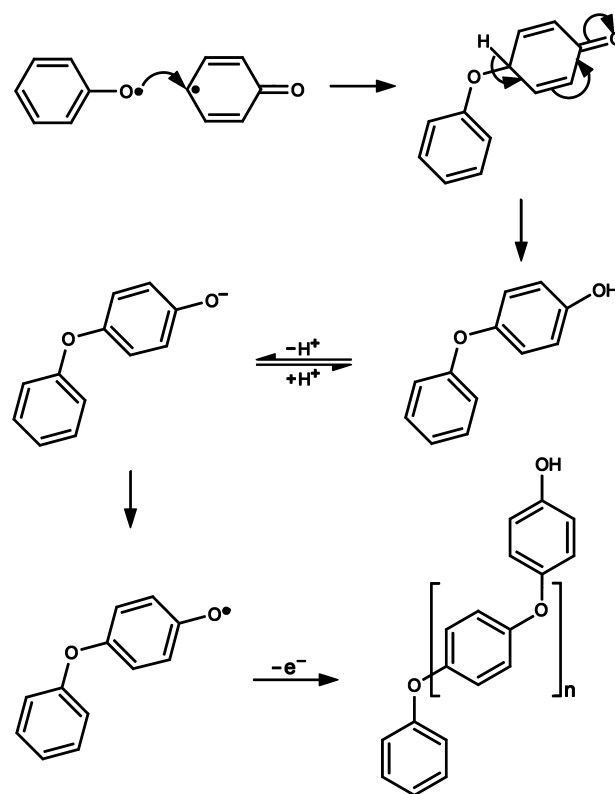
Search for Passivating Molecules. It has been known for many years that phenols can be oxidized at positive electrode potentials (approximately +0.5 V vs SCE) to yield a wide variety of reaction products.^{41–45} In general, those phenols that have hydroxy groups *ortho* or *para* to each other tend to form quinones, whereas those that have hydroxy groups *meta* to each other tend to form polymers. Phenols lacking protective side groups also tend to form polymers.

Today, there is general agreement that the early stages of phenol polymerization require the generation of free radicals.^{46,47} Although the precise mechanism is debated, most authors^{41,46–48} consider that the first step involves the removal of an electron from a phenate anion to produce a resonance-stabilized phenoxy radical (Scheme 1). The phenate anion (being negatively charged) is soluble in water, whereas the phenoxy radical (being uncharged) is not. For this reason, phenoxy radicals accumulate at the electrode surface. As their concentration rises, the radicals polymerize by pathways such as those shown in Scheme 2. Hydrogen elimination maintains the aromaticity.

Scheme 1



Scheme 2



Among the large number of phenolic compounds whose electrochemistry has been reported in the literature, one in particular caught our attention due to its ability to passivate electrodes in a single voltammetric scan. This compound is 3,5,4'-trihydroxy-*trans*-stilbene, also known as *trans*-resveratrol. It is a naturally occurring bisphenol which is synthesized by several families of plants.^{49,50} It is found in a number of common foodstuffs including grapes, cranberries, and chocolate.^{51–53} Its structural formula is shown in Figure 2. In 2006, Corduneanu et al.⁴⁹ studied the redox properties of *trans*-resveratrol by cyclic voltammetry and observed that the polymerization reaction blocked the surface of GC macroelectrodes on the first voltammetric cycle.

In our laboratories, initial efforts were aimed at determining if the polymerization of *trans*-resveratrol could be achieved on random assemblies of microelectrodes (RAM electrodes). The latter presented a particularly strong challenge to the *trans*-resveratrol system because if any of the reaction intermediates (oligomers) had been soluble in solution, then they would have been rapidly dispersed by the hemispherical diffusion flux away

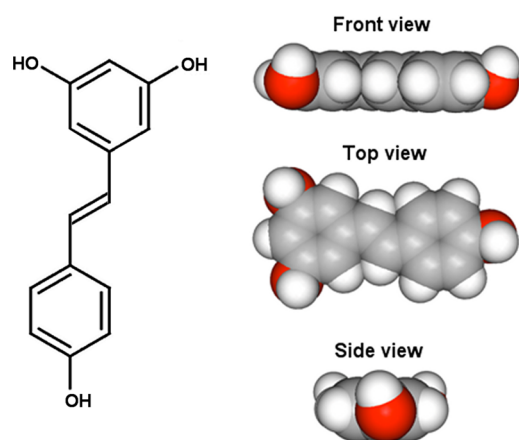


Figure 2. Structural formula and orthographic projection of *trans*-resveratrol.

from each individual microelectrode, and passivation would not have occurred. In fact, as [Figure 3](#) shows, passivation occurred on the first scan even on 3.5 μm radius microelectrodes.

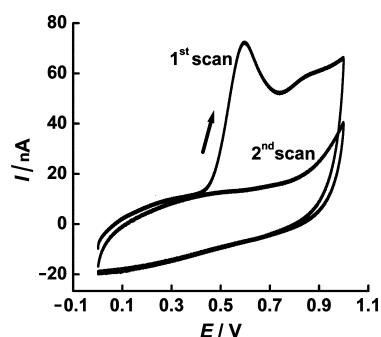


Figure 3. Cyclic voltammograms of *trans*-resveratrol recorded on a RAM microelectrode assembly. The electrolyte solution consisted of 0.5 mL of 10 mM *trans*-resveratrol in ethanol mixed with 5 mL of 10 mM acetic acid (aqueous). The scan rate was 20 mV s^{-1} . Assuming 100% conversion efficiency (i.e., no diffusional losses of oligomers), the film thickness was 11 nm.

To confirm that the films of poly(*trans*-resveratrol) were truly passive with respect to electron tunneling, both GC macroelectrodes and RAM microelectrodes were transferred into solutions containing highly electroactive redox reagents, and the cyclic voltammograms were recorded. The results are shown in [Figure 4](#).

The redox reagents that we used were bis(η^5 -cyclopentadienyl)iron(II) (ferrocene), potassium hexachloroiridate(III), and potassium hexacyanoferrate(III). The structural formulas of these compounds are given in [Figure 5](#).

It can be seen that the poly(*trans*-resveratrol) films successfully blocked electron transfer in all cases. In addition, the films were also found to have good abrasion resistance, as evidenced by the vigorous polishing needed to remove them. Indeed, the only drawback to the immediate adoption of *trans*-resveratrol as a passivating agent in carbon-based supercapacitors is its poor solubility in hydrophobic ionic liquids, which means that it cannot be deposited *in situ*. To circumvent this problem, a search was begun to identify other bisphenols that were more soluble in ionic liquids.

Passivators in Hydrophobic Ionic Liquids. Although *trans*-resveratrol is almost ideal for forming passivating films in

aqueous systems, it is insoluble in hydrophobic ionic liquids. This means that it cannot be used directly in ionic-liquid-based supercapacitors. Instead, the passivating film must be formed in a separate aqueous step and then dried before use. To avoid this unwanted complication, a screening program was undertaken to identify bisphenols that were soluble in hydrophobic ionic liquids and which could be polymerized *in situ*. The most effective compound of this type that we identified was 4,4'-(2,2-propanediyl)diphenol, also known as bisphenol A (see [Figure 6](#)).

Bisphenol A is made by condensing two molecules of phenol with one of acetone and is a well-known precursor of polycarbonate plastics and epoxy resins.⁵⁴ Unlike resveratrol, bisphenol A dissolves in hydrophobic ionic liquids, most likely because it has one fewer hydroxy group, and therefore requires one fewer hydrogen bond. Accordingly, a series of experiments was carried out to determine whether an electropolymerized film of bisphenol A could be formed on a carbon electrode in a hydrophobic ionic liquid (BTM-TFSI), and, if so, whether this film could also prevent unwanted faradaic reactions.

Initially, the ionic liquid was saturated with bisphenol A (0.2 M), and the electrode potential was cycled at 20 mV s^{-1} for five cycles on a RAM electrode. The result is shown in [Figure 7](#). It is evident that the *in situ* polymerization of bisphenol A could be successfully achieved. Next, in order to confirm its passivating power, the voltammetric response of the same system was recorded on a RAM electrode with ferrocene already present. The results are shown in [Figure 8](#). Within two scans the ferrocene reaction was fully blocked.

Unfortunately, our joy at finding that poly(bisphenol A) was an excellent passivating agent for carbon in a hydrophobic ionic liquid was soon tempered by the realization that the monomer of bisphenol A might be a human health hazard. In recent years, reports have appeared which suggest that bisphenol A is an endocrine disrupter, together with the proposal that the monomer should be banned in consumer products.^{55–58}

In the present work, the electrode surface is blocked with polymer, not the monomer, and so there is only a very small risk of exposure to the monomer. Nevertheless, the controversy surrounding bisphenol A caused us to search for a possible replacement. A molecule of somewhat different shape, which has not been implicated as an endocrine disrupter, is 4,4'-(1,4-phenylenedi-2,2-propanediyl)diphenol (bisphenol P) (CAS 2167-51-3). Its structural formula is shown in [Figure 9](#).

Assessing the Passivation Capability of Bisphenol P.

In order to test whether bisphenol P could be electropolymerized in hydrophobic ionic liquids, cyclic voltammetry was recorded on GC macroelectrodes over the range 0.0 to +2.0 V vs Ag/AgCl. Initially, the potential was held at 0.0 V vs Ag/AgCl for 30 s before being cycled between 0.0 and +2.0 V at 20 mV s^{-1} . Five cycles were recorded. The results are shown in [Figure 10](#). It can be seen that one voltammetric scan was sufficient to passivate the electrode.

Next, the ability of poly(bisphenol P) films to block faradaic reactions was studied. Ferrocene (10 mM) was dissolved in the BTM-TFSI deposition solutions, and the resulting cyclic voltammograms were recorded on GC macroelectrodes between 0.0 and +0.5 V. The voltammograms were then extended to +2.0 V to allow the monomer to polymerize. Finally, a third set of voltammograms was recorded over the range 0.0 to +0.5 V. The results are shown in [Figure 11](#). It is evident that the polymer films were strongly passive after the polymerization process.

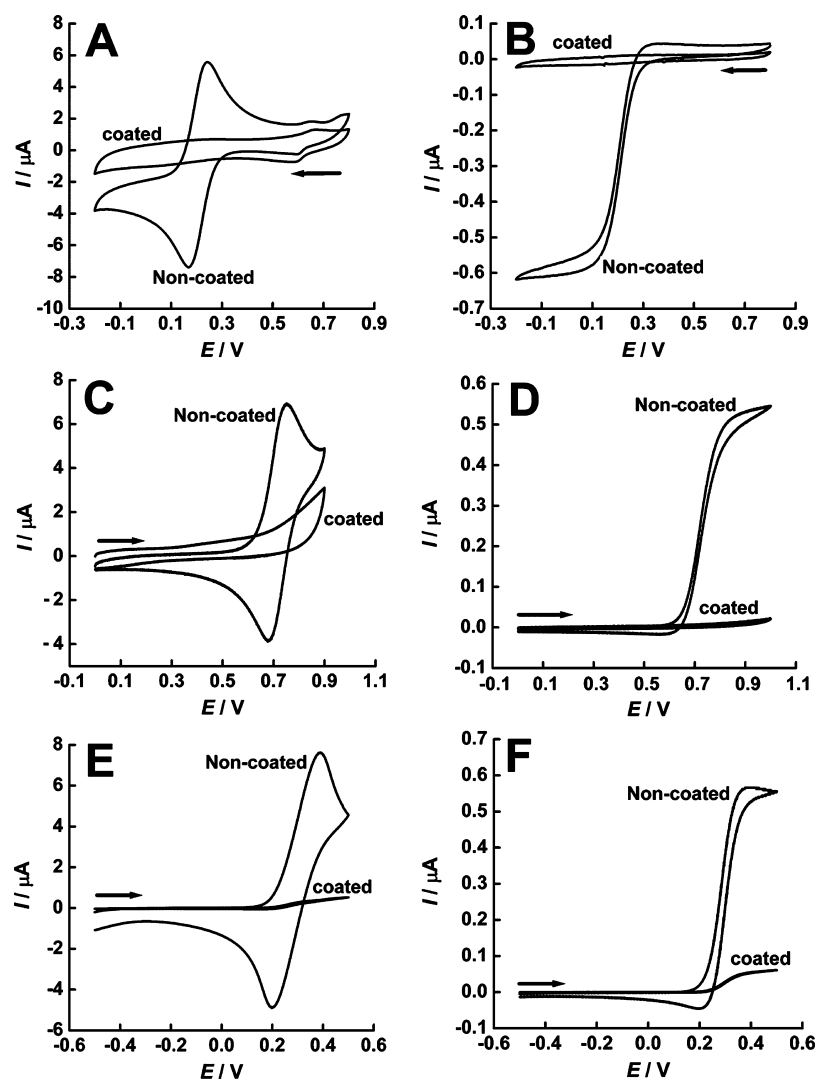


Figure 4. Cyclic voltammograms of three different redox reagents recorded on GC macroelectrodes (left) and RAM microelectrodes (right), before and after the electrodeposition of poly(*trans*-resveratrol). For (A, B), the redox reagent was 1.0 mM aqueous potassium hexacyanoferrate(III) in 0.5 M KNO₃. For (C, D), the redox reagent was 1.0 mM aqueous potassium hexachloroiridate(III) in 0.5 M KNO₃, and for (E, F) the redox reagent was 10 mM ferrocene in the hydrophobic ionic liquid BTM-TFSI. The scan rate was 20 mV s⁻¹.

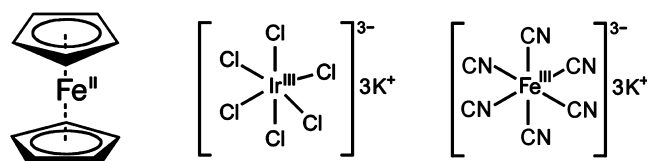


Figure 5. Structural formulas of redox reagents used to test for passivity: ferrocene (left), potassium hexachloroiridate(III) (middle), and potassium hexacyanoferrate(III) (right).

DISCUSSION

It is clear from the above results that passivation by polymer films involves a shift from *interface-controlled* conduction to *bulk-controlled* conduction. Here we discuss the quantum theory of this active/passive transition and identify the generic conditions under which it occurs.

In the presence of a thin polymer film, a high electric field is immediately established at the electrode surface. Equation 3 no longer applies, and Fowler–Nordheim kinetics dominate the

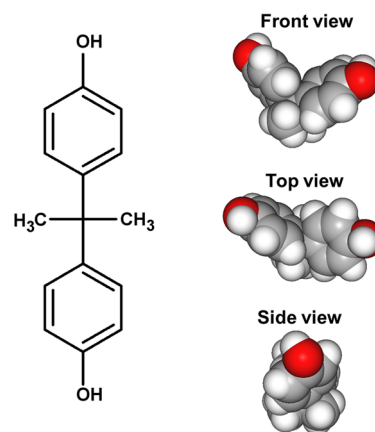


Figure 6. Structural formula and orthographic projection of bisphenol A. The bisphenols have two hydroxyphenyl functionalities separated by a bridging moiety.

interface-controlled conduction.⁵⁹ In this case the probability of tunneling takes the form

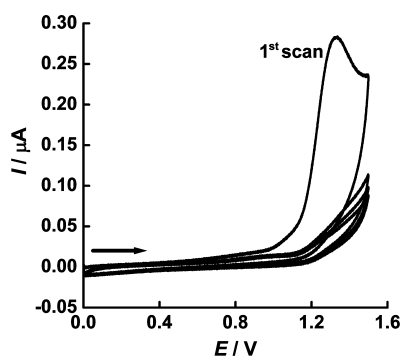


Figure 7. Cyclic voltammograms of bisphenol A (saturated) in BTM-TFSI, recorded on a RAM electrode, showing electrode passivation. The scan rate was 20 mV s^{-1} .

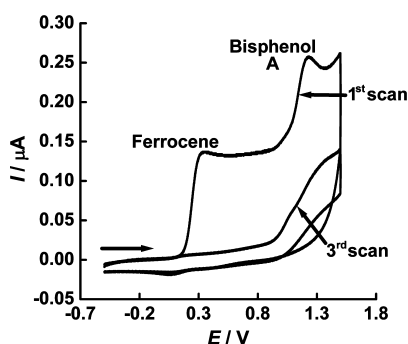


Figure 8. Cyclic voltammograms of bisphenol A (0.2M) in BTM-TFSI, recorded on a RAM electrode, with added ferrocene (10 mM). The scan rate was 20 mV s^{-1} . Passivation still occurs.

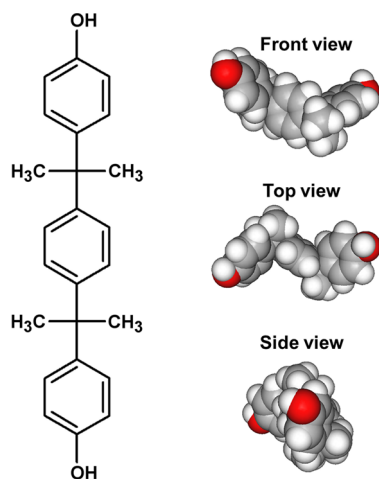


Figure 9. Structural formula and orthographic projection of bisphenol P.

$$p = \exp\left(-\frac{4\sqrt{2m} W^{3/2} d}{3 \hbar e V}\right) \quad (4)$$

where p is the probability that an electron will tunnel through the polymer, m is the effective mass of the electron, W is the electrode work function, d is the thickness of the film, \hbar is the reduced Planck constant, e is the unit charge on the electron, and V is the applied potential. If the majority of the applied potential V is dropped across the insulating film, as we expect, then the electric field strength inside the film is simply V/d , and the interface-controlled conduction increases with applied

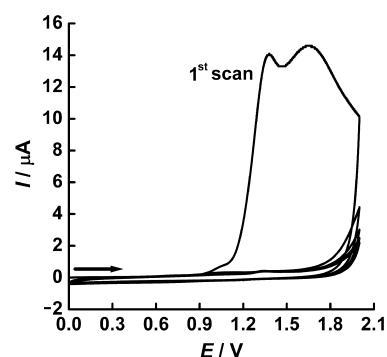


Figure 10. Cyclic voltammograms showing the electropolymerization of bisphenol P (0.5 M) on a GC macroelectrode ($r = 1.5 \text{ mm}$) in BTM-TFSI. The potential was held at 0.0 V vs Ag/AgCl wire for 30 s before cycling from 0.0 to +2.0 V at 20 mV s^{-1} for five cycles. Assuming 100% polymerization efficiency (i.e., no diffusional losses of oligomers), the film thickness was 20 nm.

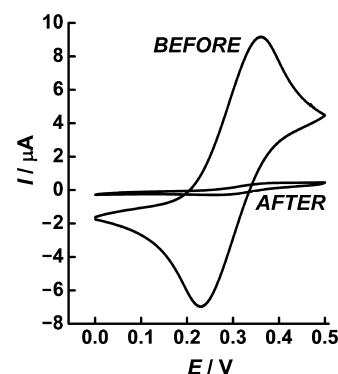


Figure 11. Cyclic voltammograms showing the knockout of the ferrocene peak (10 mM) in BTM-TFSI at $25 \text{ }^\circ\text{C}$ after the electropolymerization of bisphenol P (0.5 M). The working electrode was a glassy carbon disk electrode ($r = 1.5 \text{ mm}$). The potential was held at 0.0 V vs Ag/AgCl wire for 30 s before cycling from 0.0 to +0.5 to 0.0 V at 20 mV s^{-1} for two cycles.

potential V and decreases with film thickness d . An analogous formulation applies in the case of holes.⁶⁰

Alternatively, the probability of tunneling can be written in terms of the attenuation length α^{-1} of the wave function

$$p = \exp(-2\alpha d) \quad (5)$$

This simple equation emphasizes the distance dependence of the tunneling probability. Unfortunately, the main experimental observable, the tunneling current, is more complex and requires the evaluation of a weighted sum over the local density of states.⁶¹ Nevertheless, the resulting equation still has the elegant form

$$I \propto V^2 p \quad (6)$$

In sharp contrast to the Fowler–Nordheim kinetics, the bulk-controlled conduction is described by Mott kinetics. Mott discovered^{62,63} that the probability of an electron (or hole) hopping between two random sites in a noncrystalline (amorphous) solid depends on two parameters: their spatial separation r and their energy difference W . If these parameters are statistically independent, as they normally are, then they can be combined into a single parameter known as the “range” R between the two sites:

$$p = \exp\left(-2\alpha d - \frac{W}{kT}\right) \quad (7)$$

or

$$p = \exp(-R) \quad (8)$$

In this scenario, bulk conduction consists of a series of sequential hops through the four-dimensional space of distance and energy. Furthermore, because short-range hops are more likely than long-range hops, they tend to dominate the outcome. Mathematically, this is precisely equivalent to a model in which every site is connected to every other site by a resistor whose value is given by the inverse of the corresponding hopping probability. Unsurprisingly, the big resistors contribute very little to the total response.

If the energy distribution of sites is narrow, then the dominant factor determining the “range” is the spatial distribution of sites. From the classical theory of nearest neighbors,⁶⁴ the mean distance between a randomly selected site and its nearest neighbor is

$$\langle r \rangle = \int_0^\infty r \exp\left(\frac{-4\pi r^3 n}{3}\right) 4\pi r^2 n \, dr \quad (9)$$

which, after a little algebra, solves to yield

$$\langle r \rangle = \Gamma\left(\frac{4}{3}\right) \left(\frac{4\pi n}{3}\right)^{-1/3} \quad (10)$$

where $n = N/V$ is the volume density of vacant sites. It is evident from this result that the mean nearest-neighbor distance is only weakly dependent on the volume density (concentration) of vacant sites. An immediate corollary is that the concentration of vacant sites in the polymer film must be very low indeed to ensure that electron (or hole) tunneling is prevented.

From the above analysis, we finally reach the important conclusion that *two* criteria must be met in order for passivation to be achieved: the thickness of the insulating film must exceed the interface-controlled tunneling distance (a dimensional criterion) and the mean nearest-neighbor distance between vacant sites in the film must exceed the intrafilm tunneling distance (a compositional criterion). The particular excellence of the poly(bisphenol) polymers is that they meet both these criteria simultaneously.

CONCLUSIONS

The bisphenols form a unique group of chemical compounds with two hydroxyphenyl functionalities separated by a linking moiety. In the present work, we have shown that these compounds can be electropolymerized on carbon electrodes to yield passive films. The films are thin (<30 nm) because their growth is limited by electron tunneling. Remarkably, a single voltammetric scan is sufficient to complete the deposition process. This is seen, for example, in the cases of bisphenol A and bisphenol P.

When the films are fully formed, electron transfer to solution species is strongly inhibited, while the electrode capacitance remains unchanged. This suggests that poly(bisphenol) films may have an important role to play as passivating agents in supercapacitors. They may also find applications in other areas of technology that require thin-film passivity, such as nanostructural engineering and device physics.

In the present work, it has been noted that successful passivation requires multiple criteria to be met, especially an absence of tunneling pathways for electrons and holes and an absence of electroactive species that might otherwise diffuse through the film. In the latter case, a general theoretical model has previously been developed by Hepburn et al., and the reader is directed to their work for further discussion.⁶⁵

Because of the vast number of anion–cation combinations available today, it has become comparatively easy to modify the composition of ionic liquids to obtain certain desirable properties (such as solvent miscibility, wide voltage windows, and high conductivity). However, regardless of the properties sought, system purity still remains a matter for concern. As noted by Villagrán et al.,⁶⁶ many ionic liquids are synthesized by replacing chloride ions with complex anions. Extraction of the residual chloride then becomes a problem. The efficiency of the extraction process depends strongly on the water miscibility of the ionic liquid and the number of extractions performed. Throughout the present work, we were always careful to ensure that the concentration of chloride ions was not so great that bubbles of chlorine evolved at positive potentials, which would have interfered with the formation of the passive films. On the other hand, in the future, it remains a distinct possibility that conventional nonaqueous media might also be used for the passivation process provided gas evolution can be suppressed.

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Notes

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