No hard graft: Electrografting allows the easy formation of thin polymer films that are covalently bound to an electrode. This Review discusses the mechanism of formation of grafted polymer films and the major applications of this technique. The grafting can also be localized on doped semiconducting surfaces (see micrograph).
Electrografting: covalent bonding at metals and semiconductors

The initial charge transfer to the first monomers leads to the formation of a direct covalent bond between some surface atoms (green) and carbon atoms of the polymeric backbone (grey), followed by chemical propagation to build the polymeric chains (grey, light blue and light red).
Molecule-to-Metal Bonds: Electrografting Polymers on Conducting Surfaces


Dedicated to Doctor Gérard Lécayon

Electrografting is a powerful and versatile technique for modifying and decorating conducting surfaces with organic matter. Mainly based on the electro-induced polymerization of dissolved electro-active monomers on metallic or semiconducting surfaces, it finds applications in various fields including biocompatibility, protection against corrosion, lubrication, soldering, functionalization, adhesion, and template chemistry. Starting from experimental observations, this Review highlights the mechanism of the formation of covalent metal–carbon bonds by electro-induced processes, together with major applications such as derivatization of conducting surfaces with biomolecules that can be used in biosensing, lubrication of low-level electrical contacts, reversible trapping of ionic waste on reactive electrografted surfaces as an alternative to ion-exchange resins, and localized modification of conducting surfaces, a one-step process providing submicrometer grafted areas and which is used in microelectronics.

Introduction

Organic coatings on metals are ubiquitous today, from paints and varnishes used in the automobile industry for preventing corrosion to nontoxic interior coatings of beverage cans, from lubricant coatings for low-level electrical connectors to wear-resistant biocompatible coatings for medical devices and implants, from microelectronic chip packaging to nonstick cookware. In all applications, these coatings must be stable under harsh conditions, exhibit the required adhesive properties, protect substrates against corrosion for long periods, be either hydrophilic or hydrophobic and, last but not least, be safe for users. In the case of foodstuffs and biomaterials, these requirements are crucial, because severe health problems could arise from the failure of the coating to fulfill its specifications.[1,2]

It is thus of considerable importance to control as perfectly as possible the mechanism of formation of the coatings, and to gather as much information as possible on the strength of the linkage between the organic film and the substrate, the homogeneity and permeability of the organic film, and the stability of the coatings under severe conditions. Fundamental research is thus required not only to create new organic coatings with outstanding properties, but also to develop the characterization tools that give appropriate answers to industrial problems.

Among the numerous methods commonly used for the formation of organic coatings on surfaces, six can be emphasized for their industrial importance, the efforts made by research institutions to develop them, and their ability to provide submicrometer deposition, which is a common goal in numerous high-tech industries:

- Plasma deposition of polymers for producing highly robust polymeric coatings has been known for 50 years.[3–5] Strong chemical linkages that are assumed to be formed between the reactive species produced within the plasma and the surface of the substrate lead to highly adherent films. Since the glow discharge is a very energetic process, organic gases or vapors that are not regarded as monomers for conventional polymerization can be used. Indeed, free radicals are generated whatever the starting organic species, and the final deposit is very different from a conventional polymer film prepared by a casting technique: the plasma polymer does not contain regular repeat units, but branched and randomly terminated chains with a high degree of cross-linking. In some cases, free radicals remain trapped within the highly cross-linked structure, and their subsequent recombination results in ageing of the coatings. Plasma polymerization has been widely used for corrosion protection, scratch-resistant coatings, and antisoiling applications, although deposition rates are generally low, and film thicknesses are always higher than 1 μm.
- Spin coating is the most widely used technique for organic coatings based on polymer solutions, for example, photosensitive resins used in lithography in the microelectronics industry, antireflection coatings for flat-screen displays and television tubes, and compact discs. The range of obtained thicknesses is generally 1–200 μm, but thinner films can be produced with dilute solutions and high spinning rates. The homogeneity of the spin-coated film strongly depends on the quality of the pristine solution and the chosen combi-

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Pascal Viel, born in 1961, obtained his Ph.D. in electrochemistry from the University of Paris (France) in 1990. In the same year he joined the Commissariat à L’Energie Atomique in Saclay, to work with Dr. Gérard Lécayon on the grafting and growth of vinylic films on metallic surfaces by electropolymerization. Now his research covers many aspects of basic and technological issues of immobilized thin organic films.

Christophe Bureau, born in 1967, is an alumnus of the “Ecole Normale Supérieure”, and obtained his Master’s Degree in organic synthesis and physical chemistry in 1989 from the University of Paris XI. He was awarded a Ph.D. in Quantum Physics, with highest distinctions, in 1994 from the University of Paris VI. Dr Bureau entered the CEA in 1994 in the Chemistry of Surfaces and Interfaces group (CSI), of which he became Head in 1998. He completed a management training programme at HEC/Challenge + Business School (Jouy-en-Josas, France) in 2001–2002. He left the CEA in 2002 to found the spin-off company Alchimer S.A., which specializes in the functionalization of surfaces and interfaces in microelectronics and biomedical devices. To date Dr. Bureau has 57 refereed publications and 16 patents, at the crossroads of organic chemistry, quantum chemistry, electrochemistry, and surface science.

Guy Deniau was born in France in 1959, and studied chemistry at the University of Paris. In 1987, he joined the group of Dr Gérard Lécayon at the Commissariat à L’Energie Atomique in Saclay (CEA), where he worked on the electro-initiated polymerization of various vinylic monomers onto metallic cathode surfaces. He extended the process to various new monomers and was the first to observe experimentally the metal–carbon bond. He received his Ph.D. in chemistry in 1990. He then carried on his work in the field of electropolymerization at CEA. He contributed to the elucidation of the molecular mechanism of electrografting and was one of the major contributors to the creation of the spin-off company Alchimer S.A. in 2001.

Brigitte Mouanda received her Ph.D. in polymer chemistry at the University of Montpellier in 1984. She then joined the Commissariat à L’Energie Atomique (CEA) in Saclay, and worked with Dr Charles Rosilio on the synthesis of positive resists for photolithography. Since joining the Chemistry of Surfaces and Interfaces group in CEA in 2000, she has been working on the synthesis of new monomers for electropolymerization and chemical modification of electrografted polymers.
Electrografting of Polymers

Electrografting is a relatively new technique that allows the deposition of very thin organic films (typically between one monolayer and 50 nm) via very strong substrate–molecule links. Contrary to electrodeposition of conducting polymers, which requires a potential supplied throughout deposition to fuel the redox processes, electrografting is an electro-initiated process which requires a charged electrode only for the grafting step, but not for thickening. The resulting organic films are generally insulating, highly adherent, and optically transparent. As electrografting is mainly (but not only) a cathodic process, it can generally be applied to various metallic and semiconducting surfaces without any concern over oxide formation. This Review focuses on this technique and discusses its mechanism, its main advantages, and some selected achievements.

Electrografting: Experimental Facts

As originally shown by Lécyon et al., strongly adhesive polymer films can be formed on any conductive surface by cathodic electrodeposition from anhydrous solutions of vinyl monomers such as acrylonitrile and methyl methacrylate. Some vinyl monomers can also be electrografted at the anode by the same process. Often compared (or confused) with the anodic electrodeposition of conducting polymers from conjugated monomers such as pyrrole, thiophene, and aniline, this grafting method allows fast and reliable formation of true chemical links between organics and conducting surfaces and leads to thin, transparent, and insulating coatings. The following sections gather experimental data on this “electrografting” process.

Polymerization Peak and IR Signature of the Polymer

Electrografting occurs when vinyl monomers such as acrylonitrile (AN), methacrylonitrile (MAN), vinylpyridine (VP), and methyl methacrylate (MMA), all members of the family of electron-deficient alkenes, are submitted to reductive electrolysis with a classical three-electrode setup in an anhydrous organic medium. The spectral signature of the final grafted polymer film is very similar to that of the same polymer prepared in solution, although some fine details of reticulation and tacticity may depend on the electrolysis protocol. Although cleanliness is obviously necessary to ensure reproducible results, the presence of a metal oxide layer does not preclude formation of an electrografted film, probably because the oxide is reduced or damaged during reductive electrolysis.

Classical voltammograms recorded during electrolysis (Figure 1) exhibit a sharp peak in the cathodic domain, which corresponds to the actual reduction of the vinyl monomers. This peak is clearly of diffusional origin, but its shape is concentration-dependent. This peculiar behavior was debated in the past, but is now clearly interpreted in terms of coupling between a radical–radical coupling-initiated polymerization...
and an irreversible charge transfer. Mechanistic details are given below.

Grafted versus Nongrafted Films: Film Thickness

A striking feature of the cathodic electrografting process is that two distinct types of polymer are obtained as electrolysis products: 1) A physisorbed (or “nongrafted”) polymer, which can easily be removed by rinsing with an appropriate solvent. This physisorbed polymer film can be up to several micrometers thick depending on the monomer concentration, the solvent, and the potential-scanning protocol. 2) A “grafted” polymer, which cannot be removed from the surface by solvent rinsing or ultrasonication and is never thicker than a few hundred nanometers. The actual thickness of the film directly resulting from electrolysis (i.e., before rinsing) is strongly dependent on the solvation conditions: physisorption of the nongrafted film can be prevented if an appropriate solvent is used during electrolysis. On the contrary, using a “bad” solvent of the formed polymer during the electrolysis and rinsing steps leads to thick films containing both types of polymer, since the nongrafted polymer, which is assumed to arise from polymer chains formed in solution and entangled within the chains of the grafted polymer, contributes to the total thickness. The latter assumption is confirmed by selective poisoning of the electrode surface with sulfur-containing fragments derived from the electroreduction of thiourea, which partially inhibits the surface of the electrode, decreases the grafting ratio, and increases the amount of nongrafted relative to grafted polymer; in this case thicker films are obtained before rinsing. This indicates that, although both grafted and nongraft-
occur via precipitation of a polymer formed in solution. In contrast, as shown by Figure 3, the thickness of the grafted film that can be measured on the RDE is almost independent of the spinning rate during the grafting process. This observation strongly argues in favor of a direct grafting mechanism starting at the surface of the electrode, rather than precipitation of a polymer formed in solution.

Third, near edge X-ray absorption fine structure (NEXAFS) measurements on very thin electrografted PAN films on Ni clearly evidenced the perfect orientation of the polymer chains that are close to the metal surface: the carbon backbone is perpendicular to the metal surface, while the CN groups are parallel to it. This behavior cannot arise from precipitation of a cross-linked polymer formed in solution. Moreover, the loss in orientation observed in thicker films can be attributed to entanglement of nongrafted polymer chains originating from the solution with the oriented grafted ones.

Fourth, an in situ study with an electrochemical quartz crystal microbalance (EQCM) on the electrografting of MAN and N-vinylpyrrolidione (NVP) in anhydrous acetonitrile under cathodic and anodic conditions, respectively, clearly showed that for the latter monomer, which is known to afford only the grafted polymer because the dimer formed after desorption of the grafted radical cation is highly stable, the equivalent resistance of the quartz crystal electrode remains almost constant during electrodeposition. At the same time, the eigenfrequency of the quartz exhibits large variations. In contrast, a large increase in admittance was observed for MAN in the vicinity of the voltammetric peak maximum (Figure 4). As the equivalent resistance of the quartz crystal electrode does not change during electrodeposition, one can assume the eigenfrequency shift observed upon electrografting of NVP to arise only from a polymer film that is rigidly attached to the electrode, in the sense of the Sauerbrey equation. Indeed, PNVP films grow progressively from the surface of the electrode. As the electropolymerization mechanisms proposed for NVP and the other vinyl monomers are the same (i.e., starting from a grafted radical ion that initiates ionic polymerization), the above result can be applied to all the vinyl monomers. However, in the other cases, the large increase in admittance stems from the fast change in viscosity that follows the massive formation of oligomers in solution in the vicinity of the electrode.

Fifth, XPS measurements on very thin electrografted films exhibit a low-energy shoulder in the C1s signal. This peak cannot be observed for thicker films because it is buried under the strong C1s signals arising from the grafted polymer itself (Figure 5). The corresponding binding energy (283.6 eV) was later attributed to the carbon–nickel bond that links the polymer chain to the Ni electrode.

All these experimental data are consistent with electropolymerization starting at the surface of the electrode through strong covalent bonds between the growing oligomers and the conducting surface. The stability of this organic/inorganic interface is a key parameter in the applications of the electrografted films. Some examples will be given below.

**Electrografting: Interpretation and Mechanism**

Despite the experimental evidence described above, in situ tracking of electrografting has not been performed so far. Indeed, the various electrochemical methods that were used to follow the grafting phenomenon (e.g., classical voltammetry, voltammetry on an RDE, voltammetry on a quartz crystal microbalance (QCM)) all have the same weakness: it is very difficult to discriminate between the part of the observed signal that comes from the grafted polymer chains and that which comes from the nongrafted polymer chains.

**Mechanism**

As shown by Figure 1, the voltammograms recorded during electrografting are concentration-dependent. In a limited
range of monomer concentrations (typically between $10^{-2}$ and $10^{-1}$ M for AN in acetonitrile), multipeak voltammograms are obtained although only a single charge transfer is actually involved in the process. Moreover, single-peak voltammograms obtained at low or high monomer concentration are not of purely diffusional character.\[45\] The interpretation of this peculiar behavior was highly debated,\[44,46\] but the voltammograms were eventually shown to arise from a radical-to-radical coupling-initiated polymerization coupled to irreversible charge transfer from the electrode.\[31,47\]

The resulting molecular mechanism involves an adsorbed radical anion that initiates polymerization (Figure 6). This negatively charged species arises from charge transfer from the electrode to an adsorbed monomer molecule. Indeed, it was shown experimentally that acrylonitrile (as a prototype of electron-deficient vinylic monomers prone to electrografting) is spontaneously adsorbed and lies flat on metal surfaces\[48-50\] after displacing the previously adsorbed solvent molecules.\[10\]

The competition between solvent and monomer for adsorption on the metal surface was theoretically emphasized by a DFT-based study modeling the interactions of solvent (acetonitrile, DMF, pyridine) and monomer (AN) with the Ni(100) surface.\[46-50\] The reactant for charge transfer is thus chemisorbed neutral AN lying flat on the metal electrode rather than free AN molecules in solution. The radical anion is formed in chemisorbed state on the electrode surface through a change in conformation that was found to depend on the actual applied potential.\[48\]

**Figure 5.** XPS spectra of C1s levels of a) a nickel surface exposed to ambient atmosphere; b) a 50 nm thick PMAN film electrografted on the same nickel surface; c) a 2 nm thick PMAN film electrografted on the same nickel surface. The white arrows indicate the carbon contamination of the pristine surface, and the black arrows the carbon signals from the PMAN film. The carbon-metal bond is indicated by the hatched arrow.\[42\]

**Figure 6.** Proposed mechanism showing the competition between grafting on the surface of the cathode and polymerization in solution. Top: Reduction of the monomer gives a radical anion that grafts to the cathode to give a metastable grafted anion. The grafted anion can react with another monomer to propagate the grafted polymer chain. Bottom: The grafted anion may also be ejected from the surface and free the radical anion in solution. The radical anion evolves by radical-radical coupling into a dianion that starts to polymerize in solution to give nongrafted polymer chains.\[53\]

**Lifetime of the Grafted Monomer Radical Anion**

The key point of the proposed mechanism is the lifetime of the grafted radical ion that starts the grafted polymerization process. Indeed, this transient species is by far the least stable one involved in the mechanism, since any reaction with a monomer or an anion scavenger present as an impurity in solution will either eliminate the negative charge or move it away from the negatively charged electrode (by about 1 nm for the dimerization of AN molecules). In both cases, the Coulombic repulsion between the surface of the electrode and the grafted molecule will be abruptly lowered.

Simulations were performed to evaluate the effective potential energy hypersurface of a chemisorbed radical anion as a function of its position with respect to the surface of the cathode. The charged species was modeled 1) in interaction with its image charge within the metal, 2) in interaction with the electric field in the electrical double layer, and 3) attached to the surface by a carbon-metal bond. The second contribution was evaluated by probing the Stark-Tuning effect in the vicinity of a charged electrode on a model system: CO on Pd(100).\[51\] It was thus possible to calculate the electric field rate, that is, the relationship between the experimental electrode potential (which is a macroscopic quantity) and the actual electric field...
within the electrical double layer (which is a microscopic quantity). Finally, the effective potential seen by a chemisorbed radical anion as a function of the distance from the surface was calculated for various repulsive field strengths at the interface. The potential is fully repulsive at high field strengths \( (> 10^8 \text{ Vcm}^{-1}) \), but a well in the vicinity of the surface could be found for fields in the range \( 10^5--10^6 \text{ Vcm}^{-1} \), which ensures that the lifetime of the radical anion on the surface is finite at such fields. An explicit solution of the time-dependent Schrödinger equation for the nuclei of the adsorbed species predicts that the transient interfacial bond of the chemisorbed radical anion should be detectable in the infrared domain, for example, by second harmonic generation (SHG) or sum frequency generation (SFG) spectroscopy, and that the formation of this bond should emit photons in the same energy domain. Experimental setups are being considered along these lines.

Thus, although no direct measurement of the actual lifetime of the grafted radical anion is presently available, we can assume from the above calculations that the grafted radical anion is actually capable of accounting for the observed grafted films in the proposed mechanism.

Dynamic Interpretation of the Electrochemical Data

As grafting is the result of an electrochemical process, electrochemical measurements are a very suitable way of gathering in situ information on the mechanism. However, interpretation of the electrochemical data is blurred by competition between two distinct phenomena: growth of the grafted polymer, and growth of the nongrafted polymer in solution. As indicated in the above mechanism, both polymers are electro-initiated at the interface, whereby the latter originates from desorption of the grafted radical anion before it can react with a second monomer molecule. Thus, measuring the charge injected into the solution does not give an indication of the yield of the grafting process, but only of the efficiency of reduction of monomers.

The main reduction peak observed in typical voltammograms recorded during electrografting was originally attributed to the formation of the polymer film, the electrode being progressively passivated by the nonconducting film. However, several experimental observations show that the interpretation of the electrochemical data is not that straightforward.

First, the shape of the voltammograms is concentration-dependent. As mentioned above, multiple-peak voltammograms are observed for intermediate concentrations of the monomer, while single-peak voltammograms are observed both at low and high concentrations.

Second, the dependences of the peak current on concentration and scanning rate do not match what is normally expected for purely diffusional or purely deposition peaks.

Third, QCM measurements during electrografting clearly show that polymer uptake is detected on the surface of the QCM electrode at least 700 mV before the main voltammetric peak. This early deposition is associated with a very small variation of the resistance, which indicates negligible increase in local viscosity. When the potential approaches the voltammometric peak, both the frequency and the resistance exhibit strong modifications.

Fourth, electrografting experiments performed at potentials below and above the main reduction peak clearly indicate that grafting is disconnected from the occurrence of the peak. Grafted and nongrafted polymers, with similar spectroscopic characteristics, were observed under both potential conditions.

The above results were fully explained by considering that the fast polymerization is actually coupled with the charge transfer. The first voltammetric peak is thus the result of the massive consumption of monomer molecules in the vicinity of the electrode on formation of the polymer in solution and is not a signature of grafting itself.

Grafting without Propagation: Diazonium Salts, Macromers

Electrografting is not limited to vinylic monomers. Any cleavable electroactive molecule may in principle be linked to the electrode. Downard recently reviewed several electrochemical methods that lead to formation of covalent bonds between carbon surfaces (glassy carbon or highly oriented pyrolytic graphite (HOPG), the former being generally more reactive than the latter) and different electroactive molecules such as primary amines, aryl acetates, and alcohols (in anodic processes) and diazonium salts (in a cathodic process). In all cases radical species are formed following electron transfer from or to the carbon electrode, and the radical eventually forms a covalent bond with active sites on the electrode. Some of those methods can be successfully applied to other metal electrodes, provided the applied potential does not oxidize the electrode before the organic solute.

Although these electroactive molecules are not designed to polymerize (the reactive species formed after electron transfer are neutral and remain so after grafting), films significantly thicker than monolayers are often obtained. Indeed, excess radical species are formed in the vicinity of the electrode, and some of them can react with the previously grafted molecules. For instance, multilayer formation was confirmed by STM and XPS analysis of the final modified electrodes. However, monomolecular coverage was claimed for cathodic electrografting of diazonium salts onto Si–H surfaces, on the basis of STM analysis of the grafted film, although no specific explanation was given for the self-limiting process observed in this case.

Nevertheless, electrocleavable molecules do not give rise to any propagation reaction in solution and are therefore the designated candidates for electrochemically controlled monolayer formation, which can be viewed as an alternative to self-assembly for molecular-scale modification of conducting surfaces. As noted above for diazonium salts, hydrogenated silicon (Si–H) seems to be a surface of choice for monomolecular electrochemical modification of conducting surfaces. Alkynes, which can be electrografted cathodically or anodically, halogenated alcanes, and Grignard reagents were shown to be electrografted as monolayers in electrochemically driven processes. These recent results make electrografting a relevant candidate for surface modification of nano-objects,
with a view to fabricating nanodevices for molecular electronics. Functionalization of carbon nanotubes, based on the electroreduction of diazonium salts, was recently described.\textsuperscript{69±71} Monomolecular thickness was not attained in these cases.

Another way of grafting thick films without the drawbacks of propagating systems is to use electroactive macromers. Oligomers bearing electroactive groups at the ends of or along the main chain can be successfully electrografted to produce thick films in a single step. No propagation is expected with these very bulky molecules, but some degree of reticulation may occur between adjacent grafted chains. Aliphatic polysteres and dextran bearing pendant methacrylate groups along the main chain were recently electrografted on metal substrates.\textsuperscript{72,73} More interestingly, macromers bearing one (siloxane chain) or two (polyoxyethylene chain) methacrylate groups at the ends were successfully electrografted on gold substrates.\textsuperscript{73} This latter result shows that conducting surfaces can be readily functionalized with easily synthesized macromers to give modified surfaces covered with oligomeric species that cannot be directly electrosynthesized on the working electrode, for example, siloxane, polyoxyethylene, or polysaccharide chains.

Electrografted Films for Functionalizing Surfaces

Grafting organics on metal surfaces attributes new functionality to the final surface. As the new interface between the solid substrate and the environment, the organic film can be used as a supported reagent for any application that requires its immobilization. The following sections describe some possible applications of electrografted films on metals.

Electrografted Films as Primers

Many microsystems, including chemical sensors and biosensors, require the sensing layer to be strongly linked to a solid support. Some even require the solid support to be conducting because detection relies on an electrochemical process. Electrografting is thus a very powerful technique for immobilizing the sensing molecules on the conducting substrate by creating a primer layer to which the chemically or biologically active molecules can be easily linked through chemical couplings. For example, electrografted polymethacrylonitrile films can be used for immobilization of proteins by direct and spontaneous reaction between the nitrile groups of the film and the amino or thiol groups of the amino acids of the protein (lysine, arginine, cysteine). The final protein film is stable towards aqueous rinsing and can be used for protein–substrate recognition, as shown in Figure 7 for IgG antibody and its antigen.\textsuperscript{74}

The very high stability of the chemical link between the conducting substrate and the electrografted film makes the latter suitable for chemical modification without significant loss of matter from the surface. Nitrile groups of electrografted polymethacrylonitrile films can, for example, be hydrolyzed to amide and acid groups, or reduced to amino groups with metal hydrides. Figure 8 shows infrared reflection–absorption spectroscopy (IRRAS) data of the corresponding reaction products within the film. As very thin films were involved, the hydrolysis or reduction reactions involved the whole thickness of the electrografted films.\textsuperscript{75}

Figure 7. Protein–substrate recognition with electrografted primers: Rabbit anti-IgG (AC) was first chemisorbed onto a PMAN electrografted film (solid line). A specific antigen (AG) was then recognized by the chemisorbed antibody (dashed line). Spectrum of pure PMAN is given for comparison (dotted line).

Figure 8. IRRAS spectra of electrografted PMAN film a) after formation on gold (dotted line); b) after reduction with LiAlH\textsubscript{4} (dashed line); c) after step b) and partial reaction with glutaric anhydride (dash-dotted line); d) after step c) and reaction of the remaining amino groups with trifluoroacetic acid (solid line).

Electrografted Films as Lubricants

Extensive efforts have been made in the last twenty years to improve the performance and reliability of electrical connectors. The combination of a thin layer of gold (for its conducting properties) and a thin film of a liquid lubricant (mainly perfluoroalkyl ethers) gives very good results. However, in tribological tests under conditions of cyclic sliding, it was shown that the mean number of cycles to failure, that is, the point at which the film ceases to be operative and the friction coefficient rises abruptly (limiting lubricating regime), is merely related to the original thickness. Pretreatment of the metal surface with electrografted films proved to dramatically improve this...
behavior. Electrografted polyacrylonitrile coatings were thermally treated to render them conductive.\textsuperscript{76–78} Indeed, very low contact resistances (down to $5 \, \text{m}^2$ for a gold ball contact at $0.5 \, \text{N}$) were observed for 50 nm PAN films after annealing at $400 \, ^\circ\text{C}$ for 30 s.\textsuperscript{77}

In combination with classical lubricants these coatings exhibit remarkable properties. Significant improvements in mean friction coefficient were observed in wear experiments in which a hard gold or beryllium–copper ball was pressed onto (applied force: $0.5 \, \text{N}$) and passed over a coated nickel surface.\textsuperscript{79–82}

As shown in Figure 9, when a gold ball slides on a gold surface covered with about 200 nm of a perfluoropolyether, the lubricant layer is wiped out of the test zone after 70 to 80 cycles. In contrast, the sliding zone of a 50 nm-thick pyrolyzed electrografted PAN film covered with about 100 nm of the same perfluoropolyether remains intact after 250 cycles. It seems that the strong adhesion of the PAN film to the metal substrate allows sliding to occur between the liquid lubricant and the pyrolyzed PAN film, rather than between the lubricant and the metal. Very interesting self-healing systems based on thiol self-assembled monolayers were more recently proposed on the same lines.\textsuperscript{83–85}

Waste Disposal

Industrial liquid waste containing heavy metals is the subject of considerable ecological and economic interest, focused on the development of effective, clean, and low-cost cleaning processes. Under the ecological constraint the concept of “no liquid effluent” from industrial sites recently appeared. Polymeric ion-exchange resins, which are expensive but can be reused several times, are the most common method for reaching very low concentrations of pollutants, although large amounts of secondary effluent are created during regeneration of the resins.\textsuperscript{86} High-specific-area conducting surfaces covered with electrografted films having chelating properties can be used instead of ion-exchange resins to speed up the fixation and the expulsion of the target ions (because the interaction between the chelating groups and the ionic waste is limited to a thin film) and limit the amount of secondary effluents arising from the regeneration of the active film.

Poly(4-vinylpyridine), P4VP, thin films (typically 200 nm thick) were electrografted on surfaces such as gold films, stainless steel grids, and carbon felts.\textsuperscript{80,87} When immersed in an aqueous synthetic copper solution ($200 \, \text{mgL}^{-1} \, \text{CuSO}_4\cdot\text{SH}_2\text{O}$) the polymer swells, and complexation of copper ions by the pyridine rings results in new pyridine vibrations at 1425 and $1617 \, \text{cm}^{-1}$ in the IRRAS spectra (Figure 10). The XPS analysis of the same films allows us to estimate the coordination number between pyridine ligands and copper atoms. Ratios of up to 1:1 were obtained at high copper contents. The rigid environment of pyridine rings within the film can explain these very low coordination numbers for copper(II) ions.\textsuperscript{87}
Ammonia was used to extract the complexed copper ions from the P4VP films. Analysis by IRRAS and XPS evidenced that the films were restored to their initial composition after immersion in concentrated ammonia and rinsing. The reproducibility of this regenerative treatment is high: 150 cycles of fixation/expulsion did not cause any deterioration in the performance of the films. This outstanding stability to harsh treatment is obviously due to the very strong adhesion of the chelating film to the metal substrate, which can only be obtained by the cathodic electrografting process.\(^{[87]}\)

Experiments are now in progress to improve the efficiency of the process. The chemical regeneration step, for example, might be dropped in favor of an electrochemical process that exploits the conducting properties of the substrate to allow regent-free expulsion of the trapped ions. For this purpose, chelating groups and redox sites must be combined, as has already proven efficient in organic solution.\(^{[86,88]}\) Ion selectivity may also be obtained by using specific ligands.

**Electrografted Films: Localization**

**Electrografting on Composite Surfaces**

Localized grafting, on a micrometer or submicrometer scale, of organic substances on surfaces is a prerequisite for the design of bioelectronic devices, and a valuable component of some combinatorial screening strategies. Existing approaches typically expose macroscopic areas of a substrate to milliliter quantities of solution to attach one type of molecule, sometimes using light and specialized chemistry to carry out localized reactions. Thus, localized addressing can be obtained under electronic or photochemical radiation by using microrobotic pipetting of microdroplets, by two-dimensional electrophoresis, with printing techniques, or by microcontact. Most of those techniques require numerous processing steps and are expensive to perform.

We recently developed a cheap, one-step technique that allows localized electrografting of organic material on designed areas of a composite conducting surface. The method relies on the local work function of electrons, which can easily be tuned by patterning different conducting materials on the surface. The lateral resolution of this technique was checked with submicrometer patterns and seems to be only limited by the thickness of the coating. Resolutions compatible with real microelectronic devices can thus be obtained if thin films are used.

When the electrochemical potential was applied to the substrate by patterning different conducting materials on the surface to modify the local work function of electrons, which can easily be tuned, areas of a composite conducting surface. The method relies on allowing localized electrografting of organic matter on designed sites, but entirely conducting, substrates were then used as cathodes in the electrografting process.\(^{[87]}\)

Our experiments were performed on silicon wafers which were locally covered with thin gold films by vacuum evaporation through a mask. Interdigitated gold combs can, for example, be deposited on the silicon/silicon dioxide surface (with a thin layer of chromium as adhesion promoter). Those composite, but entirely conducting, substrates were then used as cathodes in the electrografting process. When the electrochemical potential was applied to the substrate by the gold film, the PMAN electrografted film was, as expected, detected on the gold area only. Figure 11 shows the IRRAS and XPS spectra recorded on the gold and on the silicon/silicon dioxide areas of the composite surface. No film was detected on the silicon parts. This localization clearly arises from the ohmic drop that occurs at the silicon/gold interface and prevents the potential experienced by the silicon areas reaching the threshold potential required for efficient electron transfer from the cathode to the monomer.

More interestingly, when the electrochemical potential was applied by the silicon wafer, the electrografted polymer was once again detected only on the gold areas of the surface, although the applied potential was cathodic enough to give significant electrografting on pure silicon/silicon dioxide surfaces. (Figure 12) It is thus clear that the observed localization arises from an intrinsic difference between the two materials facing the electrografting solution that makes electron transfer from the surface of the electrode to the monomer in solution more efficient for gold than for silicon/silicon dioxide. We thus believe that the effective work function of gold under the conditions of our experiments is significantly lower than the effective work function of silicon/silicon dioxide to promote faster growth on the gold areas than on the others.\(^{[86]}\) The localization may arise from preferential adsorption of charges from the electrolyte on the silicon dioxide areas, as adsorbed charges within the oxide layer are known to change the flat-band voltage in a MOS junction.

The lateral resolution of this technique was checked with submicrometer patterns and seems to be only limited by the thickness of the coating. Resolutions compatible with real microelectronic devices can thus be obtained if thin films are used. This technique opens a wide field of applications in...
many domains such as microelectronics, biomedical technology, and surface technology.

**Electrografting on Locally Doped Semiconductors**

Following the results described above, it was interesting to check the behavior of locally doped silicon substrates as cathodes for the electrografting process. Indeed, microelectronic devices such as transistors, sensors, and memories are generally based on interfaces between conducting and quasi-insulating domains resulting from lithographic steps, ionic implantation, and silicon oxide thermal growth. The microelectronics industry could benefit from a simple process that enables the local functionalization of highly or poorly doped silicon areas in a single step.

Silicon wafers (Si(100) $n$-type, bulk resistivity $5\pm 15\ \Omega\ \text{cm}$) locally doped by ion implantation ($^{31}\text{P}^+$, 50 kV) were used as cathodes for the electrografting process. The highly doped areas ($10^{15}$ atoms cm$^{-2}$) were millimeter-sized. The wafers were cleaned as usual to remove organics from the silicon oxide surface. Figure 13 shows the wafer after the electrografting of PMAN. The implantation pattern was clearly revealed by the grafting process without any mask. Profilometry on the resulting pattern indicated that the PMAN grafted film was significantly thicker on the undoped areas of the wafer. Deoxidation of the surface of the wafer before the electrografting step (HF treatment to generate a Si–H surface) resulted in the complete loss of localization: the corresponding wafer was uniformly covered by a electrografted PMAN film, like homogeneously doped silicon wafers. However, localized electrografting was observed again on locally implanted wafers that were first deoxidized by HF treatment and then reoxidized with a piranha solution (fresh 2:1 mixture of concentrated sulfuric acid and 40% hydrogen peroxide) before the electrografting step. Those latter experiments clearly indicated that the observed localization of the electrografting on silicon was governed by the resistivity of the silicon oxide with respect with the doping status of the underlying silicon.$^{[91]}$

It has long been known that silicon oxide grows more quickly from highly doped silicon than from poorly doped or intrinsic silicon.$^{[92-98]}$ The breakdown voltage of the SiO$_2$ layer was found to decrease when grown on silicon with implant-induced defects.$^{[99]}$ Silicon oxide thermally grown on As-implanted and P-implanted silicon was found to contain more suboxide and to be thicker than that on Si without implantation.$^{[97,98]}$

All these results apply to native oxide and can certainly apply to silicon oxide grown under wet acidic conditions such as piranha solution. We can thus consider silicon oxide on highly P-implanted silicon to be slightly thicker than that on nonimplanted Si. This would account for the observed results, since thicker oxide acts as an extra ohmic resistance in the electrical cell and raises the cathodic potential experienced by the corresponding area of the substrate. Thus, the implanted silicon areas generate fewer grafted radical anions than the unimplanted ones and give rise to significantly thinner grafted films.

Experiments are now in progress to generalize these preliminary results to other electrografting conditions and to measure directly the differences in the electrical behavior of the silicon oxide grown on implanted and nonimplanted areas.

**Conclusions**

This Review, although nonexhaustive, is intended to give some hints on the mechanism and the different applications of the electrografting process. After more than 20 years of basic research on this technique, we can assume to now have a good
understanding of the initiation and growth mechanisms. Future improvements will have to focus mainly on controlling the thickness of the electrografted films, if possible over the micrometer range that appears to be an upper limit for the moment, and on the improved control of localization of grafting. The time has now come for this process to be used in real industrial applications. The recent increase in patent applications in this field is a clear indication that real developments are now around the corner and should soon be launched onto the market.

**Keywords:** chemisorption · electrografting · polymers · surface chemistry · thin films


[8] See, for example, the new 128×64 OLED display by Dupont (http://www.olight.com/dupont/olight/public/index.cfm).


[17] The same features are also observed for an anodic process with N-vinylpyrrolidone (NVP), and the conclusions given in the text for cathodically electrografted films can be applied to PNVP.


Electrografting of Polymers