

Communications

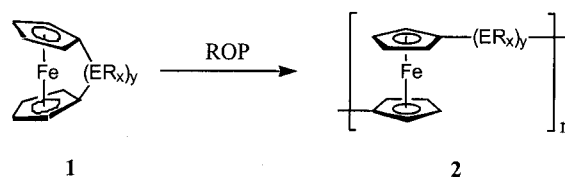
Application of Ring-Opened Poly(ferrocene)s as Protective Charge Dissipation Coatings for Dielectrics**

By Rui Resendes, Andrea Berenbaum, Goran Stojevic, Frieder Jäkke, Alexandra Bartole, Fojan Zamanian, Gerald Dubois, Charlie Hersom,* Keith Balmain,* and Ian Manners*

Numerous satellites providing communication, defense, and meteorological services are currently in the Earth's orbit, typically at altitudes of three to six earth radii. These come under the influence of charged particles (electrons, protons, and helium nuclei) originating from the surface of the sun. Satellites immersed in this ambient plasma attain electrical equilibrium via the formation of surface charges. The formation of these charges is to a large extent dependent on the development of photoelectrons originating from the surface of the spacecraft's dielectrics. However, in regions of low sunlight intensity or in periods of intense solar activities, negative charge accumulation can occur on the surface (from low energy electrons) and within the interior (from high-energy electrons) of the dielectrics comprising the satellite's thermal blankets, cable coatings, and microelectronic devices.^[1] When the potential difference between the satellite's dielectrics and the surrounding environment is such that the dielectric strength of the material is compromised, a high-energy arc discharge occurs. These arc discharges are of sufficient energy to generate magnetic interference, material breakdown, and device failure.^[2] In fact it is believed that the January 1994 and March 1996 failures on the synchronous-orbit ANIK satellites were due to such high-energy arc discharges.

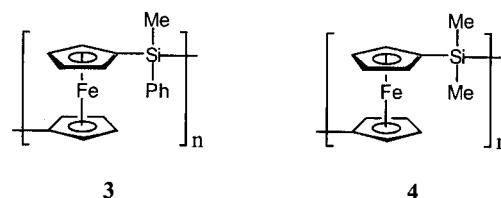
The financial implications of such electronic breakdowns are severe. For this reason a number of studies aimed at understanding the interactions of dielectrics with both high and low energy electrons have been undertaken.^[3] Also, it would be very desirable to develop a robust polymeric charge dissipating coating which, when applied to the surface of dielectrics, would remove or prevent the formation of any accumulated charge. Importantly, the coating should not possess sufficient electrical conductivity to adversely influence any nearby radio frequency devices. It should also be noted that charge dissipation materials have a wide array of other potential uses including coatings for circuit boards.

Soluble, high molecular weight poly(ferrocene)s, **2**, (E = Si, Ge, Sn, P, S, etc.) are now readily available via thermal,^[4] transition metal catalyzed^[5] or anionic^[6] ring-opening polymerization (ROP) of strained ferrocenophanes (**1**). Subsequent studies have shown that such materials possess a range of interesting properties, including high thermal stability and good processability.^[7] As a result of the interacting metal centers present in the polymer backbone, materials such as **2** (E = Si) display electrical conductivities of ca. 10^{-4} Scm^{-1} when doped with I_2 .^[8] Additionally, by varying the nature of the bridging moiety, one can tune the metal-metal interactions, and thus the electronic properties of the resulting material. As a result of these properties, pristine samples of poly(ferrocenylsilane)s, **3** and **4**, were investigated as charge dissipation coatings. In this communication, we describe our initial, very promising, results in this area.



Scheme 1.

Mylar, poly(ethylene terephthalate), was chosen as the dielectric for this study, as this material has been well studied in numerous arc discharge simulations.^[3] Here we report on findings from our investigation into the charging behavior of Mylar films, coated with thin films of **3**, under the influence of low energy (20 keV) electrons.



Scheme 2.

[*] Dr. C. Hersom
Centre for Research in Earth and Space Technology (CRESTech)
4850 Keele Street, 1st Floor
North York, Ontario M3J 3K1 (Canada)
Prof. K. Balmain, Dr. G. Dubois
Department of Electrical and Computer Engineering
University of Toronto
10 King's College Road
Toronto, Ontario M5S 3G4 (Canada)
Prof. I. Manners, R. Resendes, A. Berenbaum, G. Stojevic,
Dr. F. Jäkke, A. Bartole, F. Zamanian
Department of Chemistry, University of Toronto
80 St. George Street
Toronto, Ontario M5S 3H6 (Canada)

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Our initial experiments involved coating a 50 μm thick Mylar layer with a 30 μm thick coating of the amorphous poly(ferrocenylsilane) **3**. The coated Mylar was then exposed to a 20 keV electron beam at current densities of 1, 5, and 10 nA cm^{-2} using the experimental set up depicted in Figure 1a. No discharges were observed even after 1 h of

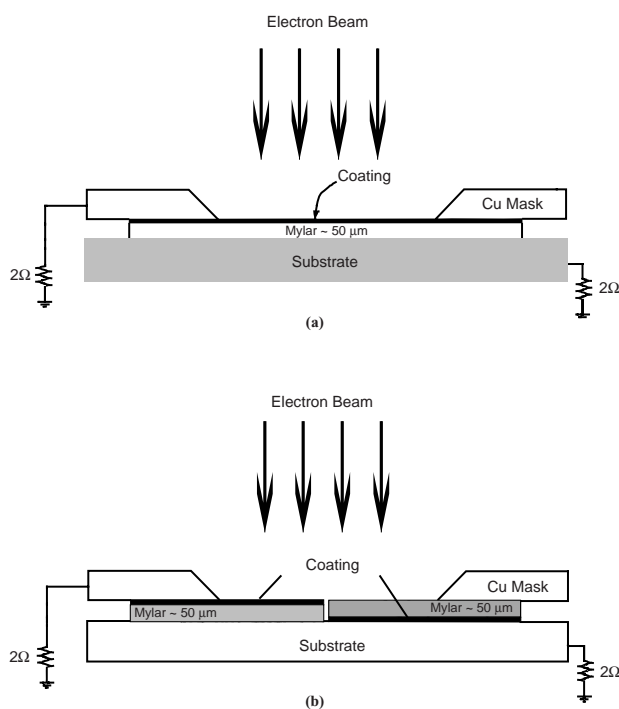


Fig. 1. Schematic representation of a) a standard specimen device and b) a split specimen device used in charging experiments.

exposure at each current density. It is important to note that the operating current densities are higher than those typically used to simulate synchronous orbit conditions (typically below 1 nA cm^{-2}). For comparison, a 50 μm thick sample of neat Mylar was exposed to similar conditions. At a current density of 5 nA cm^{-2} , a discharge was observed in the Mylar after seven minutes of exposure and repeated discharges were observed thereafter (Fig. 2a). The experiment was repeated with a Mylar sample possessing a 15 μm thick coating of **3**, and as was observed in the previous case, no discharging was apparent at all three operating current densities. In order to further substantiate our observations, Mylar samples coated with a thinner 15 μm thick layer of **3** were cut in half and one half inverted thus exposing the Mylar side of the sample to the electron beam (Fig. 1b). Under the influence of a 20 keV electron beam at a current density of 1 nA cm^{-2} , after 1 h a single discharge was observed on the side with exposed Mylar (Fig. 2b). At current densities of 5 nA cm^{-2} , five discharges were observed on the exposed Mylar side and one discharge was observed on the poly(ferrocene) coated side. Discharging in the poly(ferrocene) coated sample side became more frequent with even thinner 10 μm coatings of **3**. Significantly, in all cases where a discharge was observed on the poly(ferrocene) coated side,

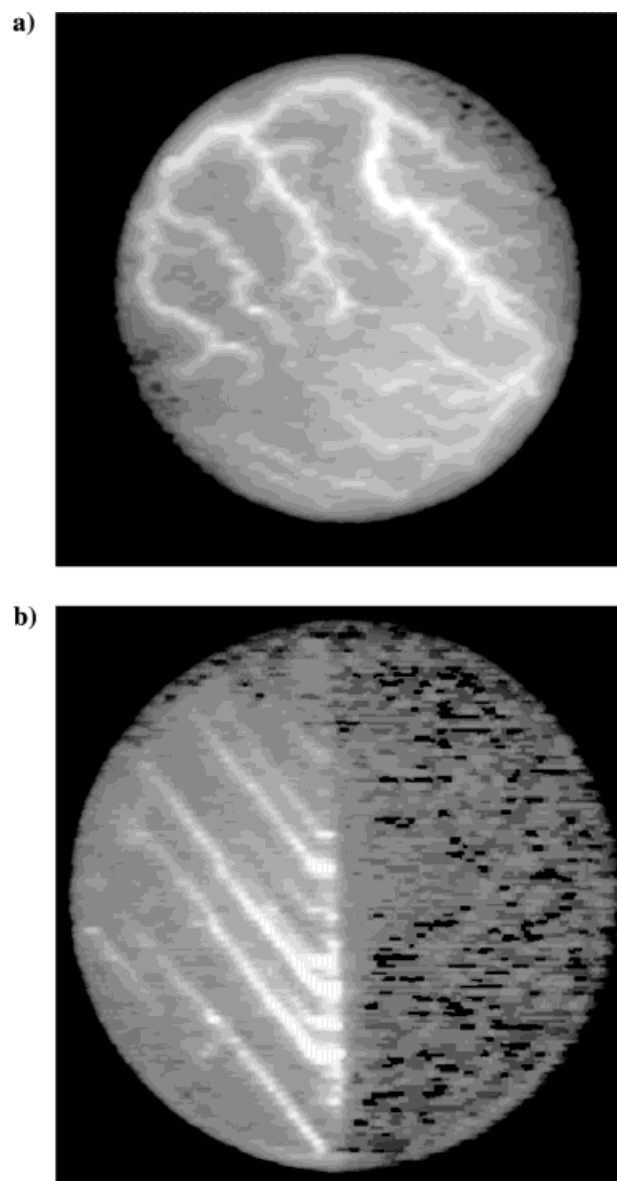


Fig. 2. Arc discharge tracks as seen in a) a 50 μm thick Mylar sample and b) a 50 μm thick Mylar sample, half (right) of which has been coated with a 15 μm thick layer of **3**. Circular aperture is 4.5 cm in diameter.

discharging appeared to originate on the Mylar half or at the coated–uncoated junction (see below).

For comparison, the charge dissipation properties of the more crystalline poly(ferrocenylsilane), **4**, were investigated under analogous conditions. When a device, comprised of a 15 μm thick coating of **4** on a 50 μm Mylar substrate, was subjected to a 20 keV electron beam at current densities of 1, 2.5, and 5 nA cm^{-2} no discharges were apparent after 1 h of exposure at any of the current densities mentioned. In order to investigate the dependence of film thickness on the charge dissipating properties, devices comprising a 5 μm coating of **4** supported on a 50 μm Mylar substrate were also investigated. While no discharging was apparent at current densities of 1 nA cm^{-2} after 1 h of exposure, discharges were observed at current densities of 2.5

and 5 nA cm^{-2} (Fig. 3 depicts a typical current pulse as recorded during a discharge). Clearly, as with **3**, the coated discharge frequency depends greatly on the thickness of the coating. This is consistent with the fact that a 20 keV electron beam is known to penetrate materials by ca. $10 \mu\text{m}$.^[3]

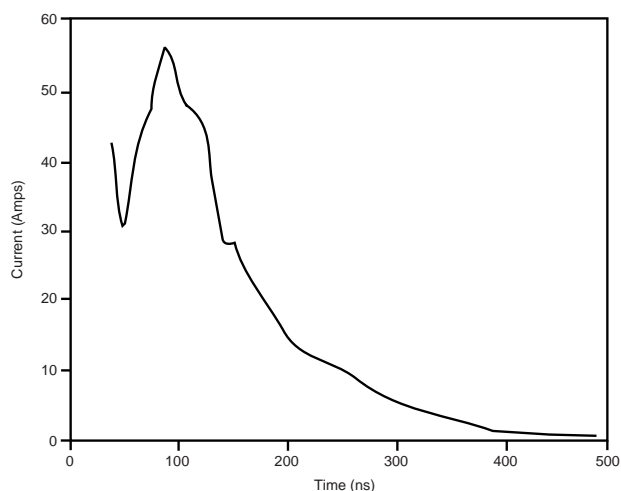


Fig. 3. Current pulse as recorded during discharge in a device comprised of a $5 \mu\text{m}$ thick film of **4** supported on a $50 \mu\text{m}$ thick Mylar substrate.

When the devices with a $15 \mu\text{m}$ coating of poly(ferrocene) **4** were cut in half and one of the halves inverted to expose the underlying Mylar substrate to the electron flux (Fig. 1b) discharges were seen consistently on both the coated and uncoated halves (Fig. 4). However, as noted in the case of **3**, where discharges were observed on the half with the exposed poly(ferrocene) coating, the discharge tracks appeared to have originated on the Mylar half or at

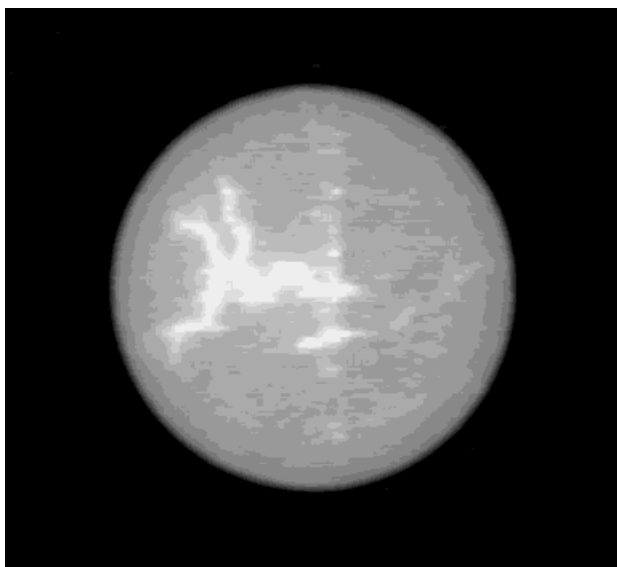


Fig. 4. Arc discharge tracks as seen in a $50 \mu\text{m}$ thick Mylar sample, half of which (right) has been coated with a $15 \mu\text{m}$ thick layer of **4**. Faint discharge tracks are apparent on the coated half. Circular aperture is 4.5 cm in diameter.

the splicing junction. We believe that it is reasonable to assume that the discharging originates at “defect” segments of the coated boundary where the polymer coating had flaked away as a result of the splicing process. Furthermore, the fact that discharging appeared much more prevalent in the halved devices based on **4** may suggest that the relative brittleness of films of semicrystalline polymer **4** (as compared to amorphous **3**) results in more of the polymer coating being flaked away from the edges during the splicing process. Further work aimed at understanding the observations and verifying this hypothesis is currently underway.

Given current knowledge of the charge transport properties of **3** and **4**, it is plausible to think of the coatings of **3** and **4** acting as semiconductors.^[8] In essence, the charge directed at the surface of the coated sample is being slowly drained to the ground. While the hole mobilities and conductivities of **3** and **4** have been studied extensively, very little is known about the electron conductivities of these materials. In one example by Yamamoto and coworkers, a poly(ferrocene)/poly(aryleneethynylene)-type copolymer with electron withdrawing substituents has been observed to possess an electrical conductivity of $10^{-5} \text{ S cm}^{-1}$ when reduced with sodium metal.^[9] This would suggest that the narrow conduction bands of a poly(ferrocene) are capable of permitting some degree of electron conductivity. The charge dissipating properties of these materials may also involve an electron scattering mechanism similar to that present in transmission electron microscopy (TEM) imaging experiments. Typical TEM experiments involve irradiating samples supported on thin carbon films with a 75–100 keV electron beam. The contrast obtained in the imaging process relies on differences in electron scattering arising from local differences in electron density. Recently, poly(ferrocene) regions of phase-separated block copolymers derived from **4** have been imaged successfully by TEM without the use of any staining techniques.^[6,7,10] This is a direct result of the presence of electron rich iron atoms in the poly(ferrocene) backbone. Given this, it is likely that an additional component of the charge dissipating mechanism in operation in **3** and **4** involves electron scattering similar to that detected in TEM imaging.

In summary, our results demonstrate that coatings of poly(ferrocenylsilane)s **3** and **4** impart a high degree of immunity to underlying dielectrics with respect to high energy arc discharges brought about by negative charge accumulation. Experiments involving the irradiation of Mylar samples, coated with thin films ($> 15 \mu\text{m}$) of **3** or **4**, with a 20 keV electron beam failed to incur an arc discharge in the underlying Mylar. These initial results suggest that materials such as **3** and **4** show excellent potential as protective charge dissipating materials. Further work is under way in our laboratories aimed at elucidating the charge dissipation mechanism, which may have both conduction and scattering components, as well as investigating the dissipating properties of related materials.

Experimental

Preparation of Polymers 3 and 4: **3** and **4** were prepared by transition metal catalyzed ROP of [1]siliferrocenophane monomers according to well-known procedures [5]. Molecular weights were estimated by gel permeation chromatography (GPC) calibrated to polystyrene standards. For **3**: $M_w = 4.3 \times 10^5$, Polydispersity Index (PDI) = 1.9. For **4**: $M_w = 2.9 \times 10^5$, PDI = 1.6.

Preparation of Devices: Devices based on **3** and **4** were prepared by coating a 50 μm thick Mylar film with 1.5 mL of a 15 wt.-% solution of **3** or **4** in toluene. Film applications were accomplished with the use of a motor-driven blade applicator (designed and built in-house) using a stainless steel blade (Paul N. Gardiner Company) with a 0.25 mm slit opening driven at a constant linear velocity of 1 cm s^{-1} . Mylar films (type A Mylar, Dupont) were purchased from Cadillac Plastics.

Arc Discharge Simulations: Films of **3** and **4** supported on Mylar were placed underneath a copper mask possessing a 4.5 cm diameter circular aperture. The electron beam was generated using a modified SEM operating at variable filament currents. Discharge images were captured with a Tektronix model C1002 CCD video camera, which is fed into a Sony model EVO-9800 Hi8 videocassette recorder. Discharge current pulses were measured using a Tektronix model 72500 transient digitizing oscilloscope.

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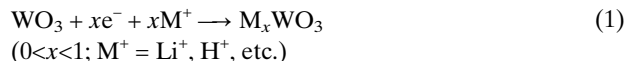
“Writing–Reading–Erasing” on Tungsten Oxide Films using the Scanning Electrochemical Microscope**

By Iva Turyan, Ursa O. Krasovec, Boris Orel, Tsiara Saraidorov, Renata Reisfeld, and Daniel Mandler*

The developers of storage systems that are capable of “writing–reading–erasing” information are constantly seeking new alternatives in order to increase memory and speed.^[1,2] Most systems are based on two-dimensional arrays where the smallest commercial memory cells are of the order of 0.2 $\mu\text{m}^2/\text{bit}$.^[3] Scanning probe microscopy

(SPM) techniques usually allow the creation of much smaller patterns; however, the access time and in particular the “writing” process is slow and, in many cases, produces only permanent changes in the surface.^[4,5] The scanning electrochemical microscope (SECM) is a SPM that emerged from the combination of the scanning tunneling microscope and ultramicroelectrodes.^[6] It comprises the electrogeneration of electroactive species at an ultramicroelectrode that is brought into close proximity with a surface. The SECM has been used to image and modify surfaces with high lateral resolution, as well as for the study of surface processes.^[7–11] We report here on a fast “writing–reading–erasing” system, which involves the local reduction of tungsten oxide thin films using the feedback mode of the SECM. The color change that accompanies the local formation of tungsten bronze makes it possible to study charge propagation inside the films.

Tungsten oxide, WO_3 , is an electrochromic material that has attracted considerable attention due to its optical properties.^[12–18] It undergoes a reversible reduction–oxidation process to form reduced tungsten oxide, i.e., tungsten bronze, of mixed valency (Eq. 1).



Both states differ in their conductivity^[12–14] as well as their color.^[15,16] While WO_3 is transparent and has low conductivity, M_xWO_3 varies between deep blue with n-type semiconductor characteristics ($x \sim 0.3$), to bronze with semimetallic properties ($x \sim 0.9$). The transition between the two states occurs at potentials between 0 and (–1) V vs. Ag/AgCl depending on the supporting electrolyte, the concentration of M^+ , and the preparation procedure of the film. The rate of coloration is limited by the diffusion of M^+ inside the film and therefore depends on the film thickness and permeability.^[17,18]

This encouraged us to develop a system that aims at the micropatterning of tungsten oxide films using the SECM. Figure 1 shows the steady-state feedback currents attained at a biased ultramicroelectrode approaching unbiased, oxidized tungsten oxide films. The films were prepared by the sol–gel method and dip-coated on conducting SnO_2 glasses.^[19,20] Clearly an increase of the steady-state current at the ultramicroelectrode, so-called positive feedback current, is observed in the case of electrogenerating a strong reductant, e.g., methylviologen radical cation, MV^+ . On the other hand, a decrease in the feedback current, i.e., a negative feedback current, is detected while approaching the film and generating an oxidant such as Fe^{3+} . The positive feedback current must be due to the oxidation of MV^+ on the electrode surface as a result of the local reduction of tungsten oxide (Eq. 1). Nevertheless, the positive feedback current was not followed by any local coloration of the film, suggesting that although electrons are efficiently injected into the film, they are not followed by cation incor-

[*] Dr. D. Mandler, Dr. I. Turyan, Dr. T. Saraidorov, Prof. R. Reisfeld
Department of Inorganic and Analytical Chemistry
The Hebrew University of Jerusalem
Jerusalem 919094 (Israel)
Dr. U. O. Krasovec, Prof. B. Orel
National Institute of Chemistry
Hajdrihova 19, 1000 Ljubljana (Slovenia)

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