

Kinetics of Water Transport in Organic Coatings

Electrochemical impedance spectroscopy (EIS) is frequently used to evaluate the capacitance of organic coatings in aqueous solutions. During aqueous exposure, water ingress leads to an increase in the measured coating capacitance due to the higher dielectric constant of water. Thus, by exposing a dry coating to an aqueous solution and monitoring the capacitance as a function of time, the rate of water ingress and the effective diffusivity can be quantified. However, for obvious reasons, this same methodology cannot be extended to evaluate the rate of water egress from the coating. Recently, room temperature ionic liquids have become available which enable water egress from the coating to be measured. These materials are essentially ionically-conductive salts that are liquid at room temperature. In a recent report, 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ($C_{10}H_{20}F_3NO_3S$), was utilized. Due to the hydrophilic nature of $C_{10}H_{20}F_3NO_3S$, exposure of a wet organic coating to this liquid led to extraction of absorbed water from the coating, resulting in a decrease in coating capacitance as a function of time. By monitoring this decrease, the diffusivity for water during egress was quantified. A bisphenol-A based epoxy coating was exposed to an 0.05 M NaCl solution and the kinetics of water ingress were quantified, after which the coating was immediately transferred to the ionic liquid where the kinetics of the water egress process were measured. The diffusivity for ingress was found to be lower than that for egress.

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Photonic Reporting of Electrochemical Reactions

Electrochemical experiments often involve application of a potential to an electrode and measurement of the resulting current. This approach works well for single-cell experiments, but microfluidic-based electrochemical methods have opened up the possibility of fabricating tens or hundreds of electrochemical cells on a single chip and simultaneously carrying out an equivalent number of electrochemical reactions. In such cases, detecting the output of these cells in parallel by dc measurements becomes cumbersome. Sun and Crooks at Texas A&M University recently reported an alternative approach based on measurement of a photon flux that is proportional to the current. In this approach, a conventional electrochemical cell is connected in series with an electron-to-photon (EP) converter. The EP converter can be either an electrogenerated chemiluminescence (ECL) cell or a light-emitting diode (LED). Compared to ECL, the authors found that LED reporting of electrochemical

reactions has the following performance benefits: lower threshold current for photon emission, more efficient and stable electron-to-photon conversion, and larger dynamic range. A significant outcome of this study is that it is possible to use an array of LEDs to simultaneously report electrochemical processes in ten thin-layer electrochemical cells. The ability to monitor multiple electrochemical reactions simultaneously, without the need for a potentiostat, current measurement system, or reference electrode, may make this useful for array-based sensing and combinatorial screening applications.

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Deposition of a Polyaniline Nanowire Network

Electrochemical capacitors, or supercapacitors, have attracted a great deal of attention as potential alternatives to batteries in certain applications due to their high power and excellent cycle life. However, the specific energy is an order of magnitude lower than batteries, thereby limiting their usefulness. Redox supercapacitors, which utilize the pseudocapacitance arising from reversible faradaic reactions, offer promise for increasing the energy. Spreading the redox reaction over a high surface area, and ensuring small length scales, could result in a device that has both high energy and high power. Researchers from Kyushu University and the Japan Science and Technology Agency are pursuing this goal by electrochemically depositing nanowires of polyaniline on a stainless steel substrate. The electrochemical deposition decreases the complexity involved in traditional nanostructure synthesis techniques, providing hope for a lower cost. The resulting capacitors demonstrate excellent capacitance of 818 F/g at 1 mA/cm². While the capacitance decreases at higher rates, the decrease is significantly smaller than the non-wire form of polyaniline. At the specific energy of 68 Wh/kg, a specific power of 16 kW/kg was obtained. Cycling data showed a decrease in capacitance in the first 100 cycles after which the value was constant up to 1500 cycles.

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Ultrathin HfO₂ Gate Stack with TaN/HfN Electrodes

High-k dielectrics will be required to replace conventional SiO₂ gate dielectrics in advanced complementary metal oxide semiconductor (CMOS) circuits. HfO₂ is considered as one of the most promising candidates for these applications, and a great deal of effort has been directed at development of HfO₂ gate stacks with low leakage currents and an equivalent oxide thickness (EOT) of < 1 nm. A research team from Peking University, IMEC, the National University of Singapore, and the

University of Texas at Austin has reported the fabrication of ultrathin, high-quality HfO₂ gate stacks. The authors used NH₃-based nitridation prior to HfO₂ deposition to suppress interfacial oxidation at the Hf/SiO₂ interface. TaN/HfN metal layers were subsequently deposited on the HfO₂ by reactive sputtering. The nitridation process provides excellent thermal stability of the oxide (with respect to thickness and leakage current) during post metallization annealing at temperatures as high as 1000°C. The gate stacks produced in this work showed an EOT of 0.65 nm with gate leakage of 0.3 A/cm² at V_{FB}-1 V. The authors state that these are the thinnest EOT and lowest leakage current values ever reported for high-temperature fabricated HfO₂ devices.

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Photoluminescent Properties of Alq₃ Films

Tris(8-hydroxyquinoline)aluminum, Alq₃, is an electroluminescent molecule that has been widely investigated since its discovery nearly two decades ago. Long lifetime organic light-emitting devices based on Alq₃ depend on encapsulation to protect the molecule from moisture and oxygen. However, devices still eventually degrade. A team of researchers from ENEA Frascati Research Center, Harvard University, and Nagpur University conducted experiments aimed at better understanding the processes occurring in the film during device degradation. They made photoluminescence measurements of the sample films at designated times during a greater than yearlong period. One set of films was kept under dark conditions and exposed to laboratory atmosphere and humidity, while another other set was stored in a dry box. Four contiguous groups of data, each having independent amplitude and time constant parameters and thereby having physical meaning referring to a hierarchical progression for the decay of the film, were found to satisfactorily describe the entire set of emission peak intensity versus time data. The authors proposed a model based on an amorphous film comprised of a close packing of droplets of Alq₃. The first decay group represents degradation of the surface molecules of the droplets. The other three species are interior to the droplets and are subjected to different (and yet undetermined) mechanisms of degradation.

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