

Electrochemical effect of electrostatic charges at insulators

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The generation of electrostatic charge from the contact of two different insulators (dielectrics) such as Teflon and glass is generally known as triboelectric effect^{1,2}. This phenomenon was first observed by Thales of Miletus, who first suggested the word 'electricity' which is derived from the Greek word for amber, *ēlektron*. He was rubbing amber with wool and observed sparks during the rubbing process. Despite its long history³, the charge identity (electron or ion) on rubbed insulators is still not properly understood. The possible chemical effect of electrostatic charge has not been widely studied. Recently, an ordered series has been established by which one can predict the type of electrostatic charge (positive or negative) on the rubbed dielectric material due to contact process. This series is known as triboelectric series¹.

Chongyang Liu and Allen J. Bard from the Department of Chemistry and Biochemistry, University of Texas, Austin, USA have drawn inspiration from the contact electrification of insulators and have demonstrated the nature of the electrostatic charges produced on mechanical rubbing of Teflon (polytetrafluoroethylene) with lucite (polymethylmethacrylate)⁴. They had carried out various electrochemical (redox) reactions on the mechanically rubbed Teflon including hydrogen evolution from acidic solution, or electrochemical deposition of copper (Cu) metal. These charges were directly identified by them as electrons rather than ions. They found a unique tool for measuring the charge density, energy and spatial distribution of charges through analysis of reaction products. Thus, the charges generated by contact electrification on dielectrics had been identified and the precise determination of the charge density has solved the long-standing problem.

The Teflon surface was rubbed by hand with another substance such as metal, glass, nylon or lucite. It became

negatively charged as determined with an electrometer, while the lucite became positively charged. All the electrochemical experiments were carried out after the completion of rubbing, to avoid the possible occurrence of tribochemistry, which deals with the relation between mechanical work and mass transformation.

When the Teflon pieces were placed in an aqueous acidic solution after rubbing with lucite, the pH of the solution increased and there was evolution of hydrogen gas. This was detected by ultra-high vacuum (UHV) mass spectrometry using D₂O inside a glove box. This indicates that electrons are present on the rubbed Teflon surface and it causes reduction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) at the electrode–electrolyte interface. Unlike a conventional two-electrode electrochemical cell, this reduction causes an excess of hydroxide ions (OH⁻) as anions in the solution with an increase in the pH of the solution. If the pH change is attributed totally to the reduction of H⁺, then a surface charge density of $\sim 10^{15} \text{ cm}^{-2}$ would be found. This was calculated from Faraday's law of electrolysis. However, the actual charge density was found to be less than this value due to surface roughness of Teflon. In the second experiment, Liu and Bard used the rubbed Teflon in an aqueous solution of 1 mM CuSO₄ and Cu metal was electrodeposited on Teflon. It was confirmed by energy-dispersive X-ray spectroscopy (EDS). No Cu peak was observed on unrubbed Teflon, but Cu peak was observed in case of rubbed Teflon. This further confirms the presence of electrons due to contact electrification on the rubbed Teflon surface. From the analysis of products, the charge density was found to be $7 \times 10^{14} \text{ cm}^{-2}$, which was similar to the value obtained from the previous experiment. In addition to this, Cu deposition was amplified by depositing palladium (Pd) first in a pre-determined pattern, followed by electrodeless deposition in a Cu plating bath

containing CuSO₄, KNaC₄H₄O₆, NaOH and HCHO to produce Cu lines. Therefore, this process can be potentially useful in microelectronic application utilizing the low dielectric constant and good thermal stability of Teflon. Similarly, reduction of Fe(CN)₆³⁻ into Fe(CN)₆⁴⁻ was also performed on charged Teflon. They observed charged Teflon-generated chemiluminescence in the system of Teflon (-)/Ru(bpy)₃²⁺/S₂O₈²⁻. This phenomenon, which was analogous to electrogenerated chemiluminescence (ECL)^{5,6} is known as electrostatic chemiluminescence (ESCL). Since, ECL is a sensitive method used to determine low levels of species in solution at picomole level, ESCL can be complementary to ECL techniques in analytical applications⁶.

It may be possible to obtain a wide range of electrode potentials rubbing together different materials and a table similar to normal electrode potentials and triboelectric series can be constructed. We speculate that this phenomenon can be potentially applied to other dielectric materials of different shapes and sizes to investigate various electrochemical processes including industrial and physiological processes.

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