STUDY OF INTERFACIAL ORGANIZATION OF ROOM TEMPERATURE IONIC LIQUIDS AT NANOSTRUCTURED CARBON ELECTRODES

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Carbon’s uniqueness stems from its ability to bond with itself and form stable allotropes with incredibly diverse physical, chemical, electrical, and electrochemical properties. These allotropes include single- and poly-crystalline diamond (sp³), glassy carbon (sp²), and diamond-like carbon (hybrid sp²/sp³). Owing to their easy availability and low cost, wide potential window, low background current, and resistance to fouling, these allotropes find extensive applications as electrode materials in electroanalysis, energy storage technologies, and electrochemical separations. For their optimal use, it is critical to understand and control the parameters that affect their electrochemical behavior. Over the last three decades, structure-property-function relationships for carbon electrodes have been established in traditional aqueous electrolytes. However, there exists a knowledge gap when it comes to the novel electrolytes called room temperature ionic liquids (RTILs).

RTILs are liquid salts solely made of charged cations and anions. They contain no solvent. They are finding ever-increasing use as electrolytes due to their excellent properties like wide thermal and electrochemical potential window, negligible vapor pressure, and good ionic conductivity. Since RTILs are highly charged media without any solvent, their response to an external electric perturbation is distinct and cannot be explained by traditional Gouy-Chapman-Stern model established for aqueous electrolytes.

This dissertation focuses on understanding the interfacial organization of RTILs on microstructurally-distinct carbon electrodes as a function of RTIL chemical identity, and surface chemistry of the electrodes under applied potential. The physical, chemical and electronic properties of glassy carbon, nanocrystalline
boron-doped diamond (BDD) and nitrogen-incorporated tetrahedral amorphous carbon (ta-C:N ) thin-film electrodes have been investigated and correlated with the observed electrochemical behavior of carbon-
RTIL interfaces.

Firstly, a model electrode, BDD, displaying well-defined surface states is used to probe the effect of RTIL cation size and viscosity on the background voltammetric current and capacitance. Capacitance follows the inverse trend with the RTIL size and viscosity. Next, the BDD surface is deliberately modified to vary the type and coverage of surface groups (H- vs. O-termination) to probe the effect of surface wettability on measured capacitance. Comparative measurements were made in aqueous electrolytes. For both the media, capacitance increases with the surface wettability of the electrode surface by electrolyte ions. Finally, ta-C:N electrodes of varying nitrogen content are characterized to define their bulk microstructure (sp²/sp³ content) using visible-Raman spectroscopy and electron-energy loss spectroscopy (EELS), and surface chemistry using X-ray photoelectron spectroscopy (XPS); all of which revealed that the incorporation of nitrogen increases the sp²-bonded carbon content. Consistent with the sp²-carbon content, ta-C:N films exhibit electrochemical properties closely aligned with those of pure sp³ and pure sp² carbon electrodes.

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