Surface Structure Dependent Anchoring of Ester-functionalized Ionic Liquids on Cobalt Oxide

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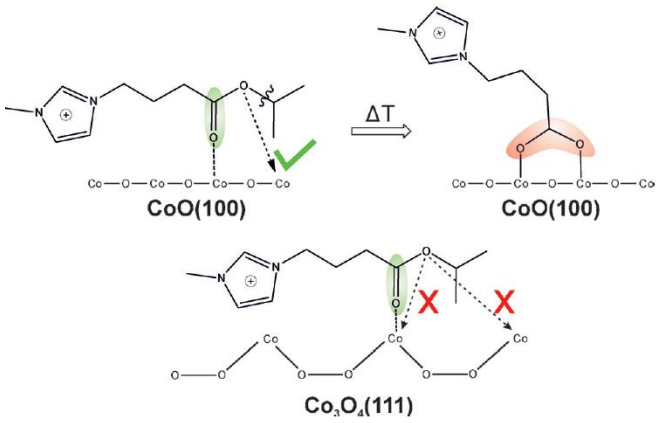
Ionic liquids (ILs) are, by definition, salts which are liquid at temperatures below 100 °C. Low vapor pressure and tuneability of other physiochemical parameters like solubility, solvation, viscosity, density or thermal stability led to various applications of ILs in catalysis, energy technology, or molecular electronics, just to name a few. Particularly, hybrid materials consisting of ILs films on supported oxides hold a great potential for applications in electronic and energy materials. The functionality of ILs in these applications relies on their interface to semiconducting nanomaterials. Therefore, methods to control the chemistry and structure of this interface are the key to assemble new IL-based electronic and electrochemical materials.



Here, we present a new method to prepare a chemically well-defined interface between an oxide and an IL film. We used the functionalized IL 3-(4-isopropoxyl-4-oxobutyl)-1-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([IPBMIM][NTf_2]) that carries an ester group at the imidazolium cation. The IL was deposited by Physical Vapour Deposition (PVD) onto atomically defined Co_3O_4(111) and CoO(100) surfaces under ultraclean ultra-high vacuum (UHV) conditions. Infrared Reflection Absorption Spectroscopy (IRAS) was applied to monitor the adsorption process and determine the interface structure of the adsorbates. The [IPBMIM][NTf_2] was found to be anchored on the CoO(100) surface through cleavage of the ester bond and formation of a bridging surface carboxylate. This anchoring reaction is thermally activated and shows high structure dependency: Whereas the carboxylate-anchored IL film is readily formed on CoO(100), the reaction does not occur on Co_3O_4(111), only weakly adsorbed ester groups are formed. [1] These differences in reactivity are attributed to the different arrangement of Co^{2+} ions on the two surfaces. We believe that this new functionalization method can be straightforwardly applied to other oxide surfaces as well, helping to prepare IL/oxide interfaces with enhanced stability and improved transport properties in electronic and electrochemical applications.

References

[1] T. Xu, T. Waehler, J. Vecchietti, A. Bonivardi, T. Bauer, J. Schwegler, P. S. Schulz, P. Wasserscheid, J. Libuda, Angew. Chem. Int. Ed. 2017, **56**, 9072-9076.