PROBING BURIED ELECTROCHEMICAL INTERFACES WITH MULTIPLEX BROADBAND SUM FREQUENCY GENERATION SPECTROSCOPY

ALEXEI LAGUTCHEV, GUO-QIANG LU, TOMOHIRO TAKESHITA, RACHEL BEHRENS, ANDRZEJ WIECKOWSKI[a] and DANA DLOTT[b], *School of Chemical Sciences, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*.

IR-visible sum-frequency generation spectroscopy has been applied to monitor vibrational resonances in an adsorbate at the surface of metal electrode under varying potential. Using IR energies in excess of 10μJ per pulse made it possible to probe adsorbed species at the electrode surface through the layer of electrolyte with controlled thickness of 25μm. Thus the common requirement of an ultra-thin electrolyte layer to reduce IR losses due to absorption in water has been largely circumvented. This allowed for drastic reduction of the layer resistance and made it possible to observe electrochemical kinetics under the conditions similar to those existing in fuel cells and other devices of practical interest. Broadband multiplex SFG configuration allowed for real-time recording of the series (motion pictures) of spectra under changing potential. Additionally non-steady state excitation by subpicosecond IR pulse made it possible to separate weak vibrational resonances from strong interfering signals by varying the delay between IR and visible probes within the time of free induction decay of the transition of interest. Two-dimensional restructuring of the adsorbate on electrode surface has been observed.

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