Negative Charge delivery in ice at 10 K: the role of surface OH radicals

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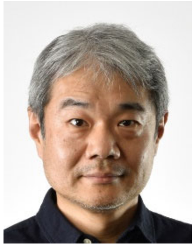

ABSTRACT

Since the study by von Grotthuss at the beginning of the 1800s, ice has been widely accepted to carry a positive current by the transfer of excess protons via H_3O^+, similar to a "p-type" semiconductor. Although the proton transfer is still a matter of controversy at low temperatures and is therefore addressed both experimentally and theoretically, this phenomenon can be well described by the Grotthuss mechanism. In contrast, although "proton-hole transfer (PHT)" has been theoretically proposed as a possible mechanism for delivering negative charges in water and ice, no clear evidence for the occurrence of this mechanism has been provided. Consequently, the concept of negative current conductivity by the PHT has remained to be confirmed experimentally for a hundred years.

Recently, we observed experimentally a negative constant current through ice at 10 K when OH radicals coexist with electrons on the ice surface [1]. From quantum chemical calculations and the experiments using the combination of photostimulated desorption and resonance-enhanced multi photoionization methods [2], the surface OH radicals were monitored with and without electrons [3], we conclude that once OH adsorbate captures an electron on the surface, the surface OH^- anions trigger the flow of negative current in ice by the sequential PHT in ice. The OH^- on the surface reproduces H_2O after proton abstraction from neighbouring H_2O. Negative current conductivity was found to be preserved even at temperatures below 50 K, where a positive current by the well-known Grotthuss mechanism is highly suppressed. The negative charge delivery by the PHT was also confirmed in other hydrogen-bonding systems like SH_2 and NH_3 solids.

REF.

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