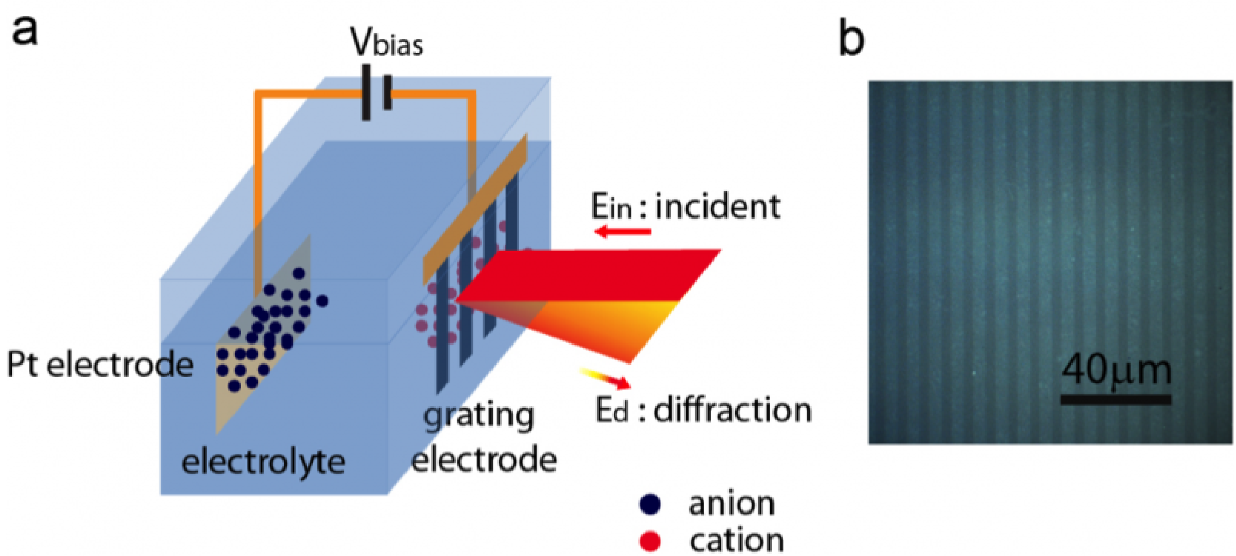
Novel diffraction spectroscopy technique to probe electrolyte/electrode interfaces

July 9 2015, by Rachel Berkowitz



Schematic illustration of the spectroscopy design with graphene grating: a)Electrochemical cell and spectroscopy configuration (Pt = Platinum); b) Optical microscopic image of a graphene grating on fused silica. Credit: Feng Wang, Berkeley Lab

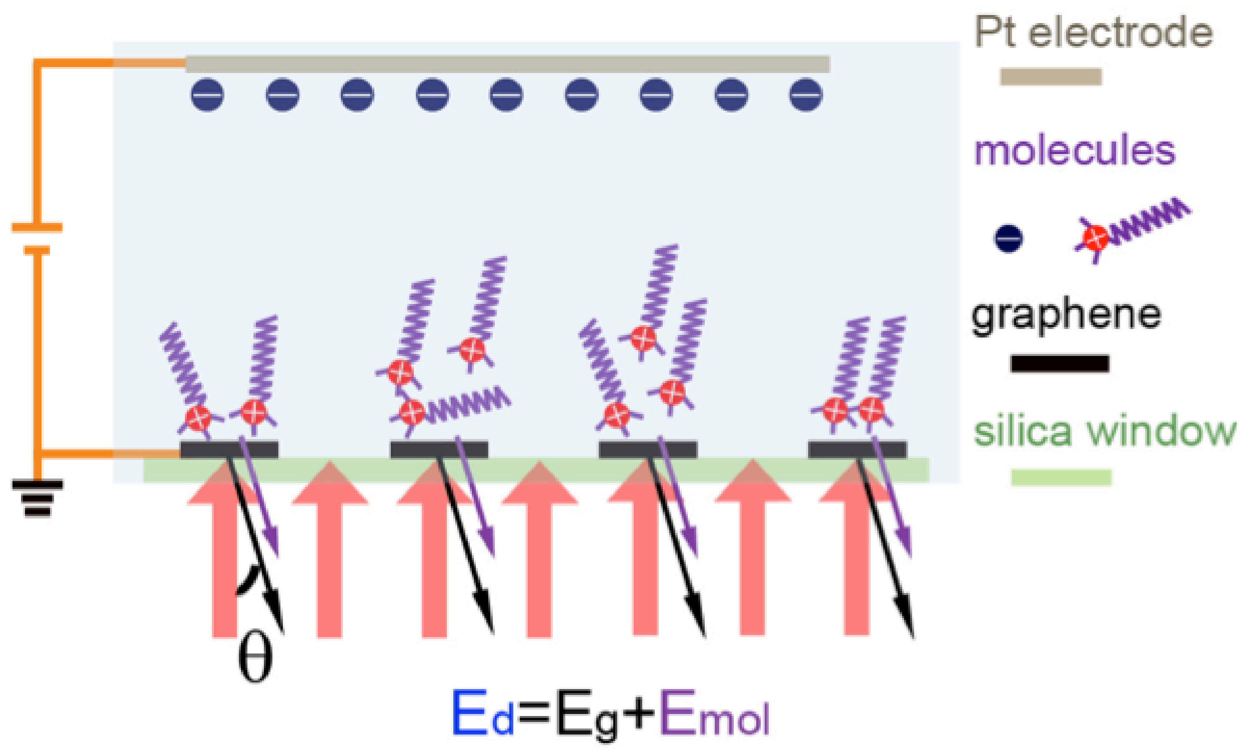
One of the most important things to understand in battery technology is the precise physical and chemical processes that occur at the electrode/electrolyte interface. However, microscopic understanding of these processes is quite limited due to a lack of suitable probing techniques. Now, researchers at the US Department of Energy's (DOE)

Lawrence Berkeley National Laboratory (Berkeley Lab) and the University of California, Berkeley, have developed a new technique that enables sensitive and specific detection of molecules at the electrode/electrolyte interface.

This new method uses diffraction from graphene gratings to overcome key difficulties associated with traditional optical spectroscopy that employs infrared probing of buried interfaces.

"Most of the electrical chemical reaction in a battery happens at the electrolyte/electrode interface, and it is important to know how tuning the electrode voltage induces field-dependent chemical processes. This requires distinction between microscopic molecule behavior at the interface, such as physical absorption, and electrochemical reaction from the bulky electrolyte solution," says Feng Wang, a physicist at Berkeley Lab's Materials Sciences Division and a member of the Kavli Energy NanoSciences Institute at Berkeley, who led this work. "Our new probing method uses diffraction from grating-like graphene electrodes. We monitor the molecule vibration modes from the diffraction signal in an in-situ, non-invasive and fast technique, taking advantage of both laser technique and graphene properties."

Wang is an author of a paper describing this research in the journal *Nature Communications*. Other authors include Ya-Qing Bie, Jason Horng, Zhiwen Shi, Long Ju, Qin Zhou, and Alex Zettl, who is also a physicist at Berkeley Lab and a member of the Kavli Institute.



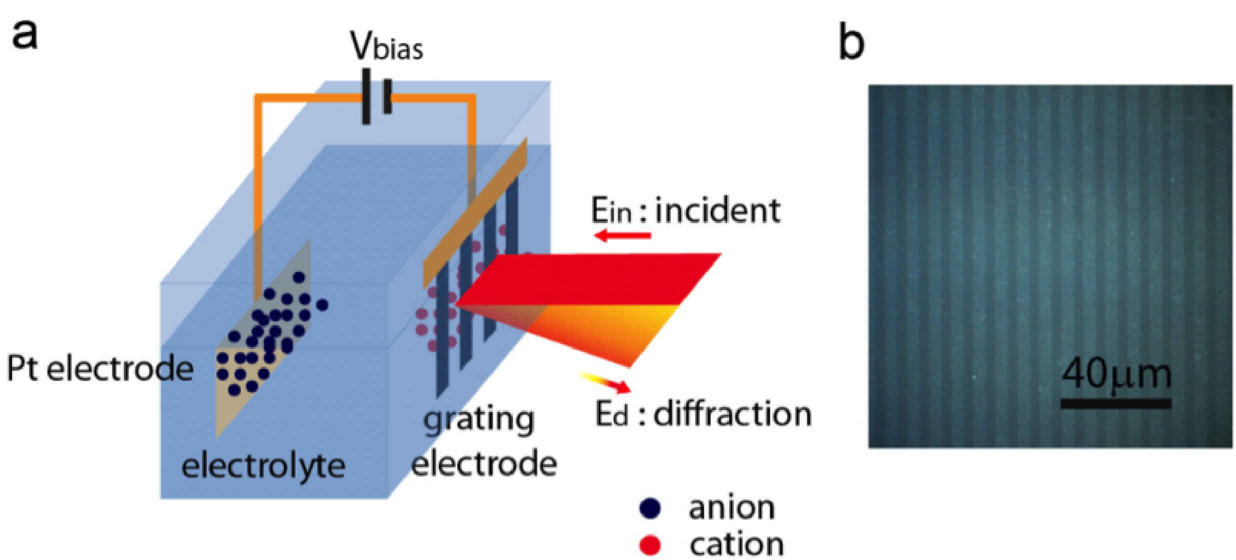
Diffraction signal is generated by periodic variation of optical susceptibility at the interface, which comes from both the graphene grating itself and different adsorbed molecules in the electrolyte double layer induced by the graphene grating. Credit: Feng Wang, Berkeley Lab

"The scientific community now has available impressive techniques for the growth, transfer, and geometrical shaping of graphene for electronic and optical application," says Zettl. Graphene is an attractive choice of electrode for interface studies because it is stable and transparent to infrared light, and is being explored for applications in supercapacitors, batteries, solar cells and displays.

The novel 'diffraction spectroscopy' uses polarized infrared radiation incident to an electrode made of graphene systematically cut into a very fine grid or grating. Together with a platinum counter electrode and aqueous electrolyte, this forms an electrochemical cell. Molecular species within the cell attach to the graphene and thereby influence the diffraction characteristics of the grating.

To investigate the molecular species at the electrolyte/graphene interface, the team measured the first-order diffraction from the graphene grating, rather than the transmission or reflection signal as in traditional spectroscopy.

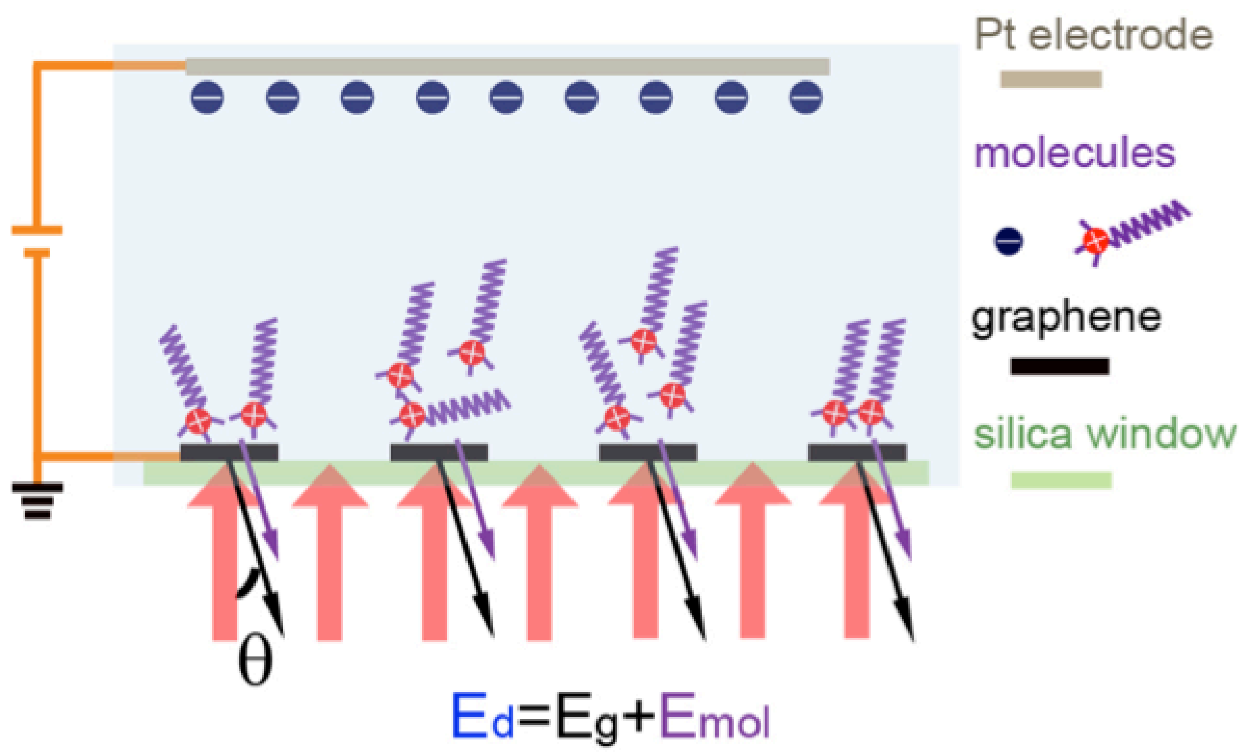
"We use the fact that the diffraction signal only probes things that have spatially periodic structures, and design our graphene electrodes to be shaped as a periodic grating. In this case, the molecules of interest are periodically distributed due to the underlying electrode grating, and most of the background signals in the traditional reflection or transmission measurement do not show up," explains Wang.



Schematic illustration of the spectroscopy design with graphene grating: a)Electrochemical cell and spectroscopy configuration (Pt = Platinum); b) Optical microscopic image of a graphene grating on fused silica.

This means that any measured diffraction originates from vibrations of adsorbed molecules in the graphene-induced electrical double layer. Relative contrast is enhanced 50 times compared with conventional absorption spectroscopy, and can detect with sub-monolayer sensitivity.

This proof-of-principle study detected CH2 vibrations from surfactant deposition on the graphene electrode as an example, but the technique can be applied to other functional groups at other infrared frequencies.



Diffraction signal is generated by periodic variation of optical susceptibility at the interface, which comes from both the graphene grating itself and different adsorbed molecules in the electrolyte double layer induced by the graphene grating.

"Beyond the vibration range of the methyl groups used in this work, there are plenty of other interesting chemical processes involving molecules whose vibration are in the infrared range. The more we know about the interface molecule behavior, the more guidance we have for device design," concludes Wang.

The Nature Communications paper describing this work is titled "Vibrational spectroscopy at electrolyte/electrode interfaces with graphene gratings."

More information: "Vibrational spectroscopy at electrolyte/electrode interfaces with graphene gratings." *Nature Communications* 6, Article number: 7593 DOI: 10.1038/ncomms8593

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