When electrochemical measurement artefacts are real

Researchers from Curtin University, the University of Murcia, Spain, the University of Wollongong, the Australian National University and the University of New South Wales have been able to reproduce and explain the often puzzling behaviour of electrons that enter or leave semiconductor materials (Vogel Y.B., Zhang L., Darwish N., Gonçales V.R., Le Brun A., Gooding J.J., Molina A., Wallace G.G., Coote M.L., Gonzalez J., Ciampi S. *Nat. Commun.* 2017, **8**, 2066). Cyclic voltammetry is the most commonly used technique to study the kinetics of electron transfer at semiconductor interfaces, providing precise control of the potential and sensitive measurement of the resulting current. Voltammograms often contain non-idealities, such as narrow waves and 'inverted' peak positions, which are often overlooked as flaws. The research team showed that 'non-ideal' voltammograms measured at Si(111) electrodes are not necessarily flawed data, but rather the manifestation of electrostatic interactions between dynamic molecular charges and the semiconductor's space–charge barrier. The so-called flaws can become very reproducible current responses under precise tuning of the electrode kinetics, indicating that either commonly used kinetic models must be revised or precautions must be taken to limit these effects. More broadly, the work has implications for the study of how static surface charges or externally applied electric fields can influence chemical bonding and reactivity, an area that is starting to attract enormous interest.