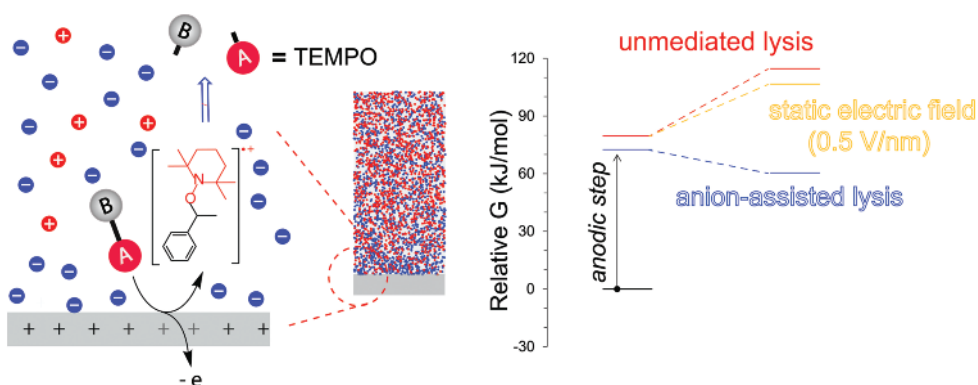


## Triggering bond cleavage with electric fields

Anodic chemistry, ionic aggregates and Debye fields  
- room temperature lysis of alkoxyamines -



Electricity has long been used in chemistry to trigger electrochemical reactions, but only recently have static electric fields been shown to catalyse non-electrochemical reactions. But implementation has to date required scanning tunnelling microscopy (STM) to orient the reagents appropriately in the electric field. Now, a team of researchers

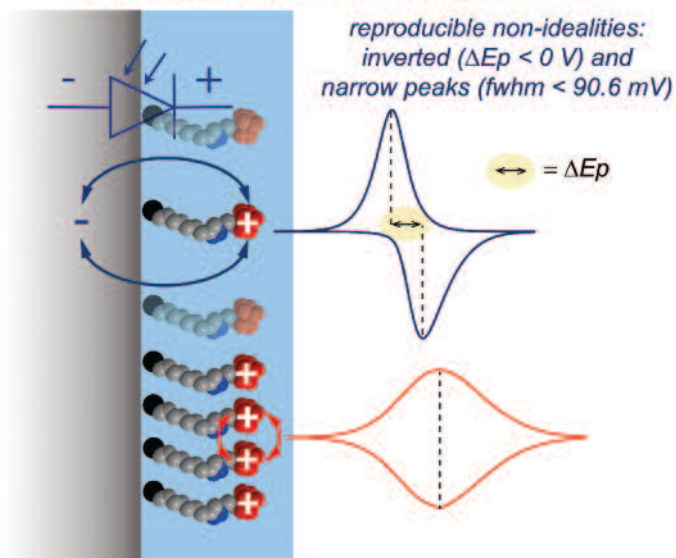
from Curtin University, the Australian National University, the University of Wollongong, ANSTO, the Silesian University of Technology, Poland, and the University of Murcia, Spain, has shown that electrostatic factors contribute to the catalysis of a chemical process that follows an anodic reaction in an electrochemical cell (Zhang L.,

Laborda E., Darwish N., Noble B.B., Tyrell J.H., Pluczyk S., Le Brun A.P., Wallace G.G., Gonzalez J., Coote M.L., Ciampi S. *J. Am. Chem. Soc.* 2018, **140**, 766–74). Using STM, the researchers first showed that thermally stable alkoxyamines underwent room-temperature homolysis when exposed to an appropriately aligned electric field. Then, they showed that cleavage also occurred at an electrified electrode–electrolyte interface, albeit with an important twist. The alkoxyamines first underwent one electron oxidation prior to exceedingly fast cleavage into carbocations and nitroxides, the latter driven by the presence of an external static field. Electrochemical cleavage was shown to proceed for free alkoxyamines in solution, and for alkoxyamines tethered to a silicon electrode, the latter providing a strategy for in situ generation of surface-tethered nitroxides or surface-tethered carbocations.

## 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

**When flaws are accounted for: semiconductor space-charge effects on the activity of surface charged molecules**



able to reproduce and explain the often puzzling behaviour of electrons that enter or leave semiconductor materials (Vogel Y.B., Zhang L., Darwish N., Gonçalves 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.