

# Century-old electrochemistry law gets update

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Credit: Leiden University

The Gouy-Chapman theory describes what happens near an electrode when it is in contact with a salt solution, but this description does not match reality. Researcher Kasinath Ojha, assistant professor Katharina Doblhoff-Dier and professor Marc Koper present a new version. "The next generation of textbooks on electrochemistry is going to look different."

When you look inside a [fuel cell](#), one of the things you will see is an [electrode](#), often made of platinum. This piece of metal is in contact with a [salt solution](#), which contains positively and negatively charged particles called ions. If you were to zoom in on the interface between the electrode and the salt solution, you would perceive all kinds of

interactions. At the surface of the electrode, a shortage or abundance of electrons exists. This charge attracts the ions from the salt solution so that they collect in the liquid near the electrode. This structure of charges is called the electrical double layer. If you alter the voltage in the device, the double layer changes as well. The Gouy-Chapman [theory](#) describes how this charge is distributed exactly.

## **Theory does not match reality**

But Marc Koper, Professor of Catalysis and Surface Chemistry, together with researcher Kasinath Ojha and associate professor Katharina Doblhoff-Dier, discovered that this description does not match reality. "It is a [classical theory](#) that is over a hundred years old, verified in the 40s and 50s of the twentieth century by David Grahame with mercury as the electrode, because measurements with solid metals were more difficult," says Koper. "People assumed that the theory was also applicable to solid metals such as platinum, but it turns out that this is not the case." Koper's research team presented an improved theory in the scientific journal *PNAS*.

## **Important quantity is nowhere to be found**

Using the Gouy-Chapman theory you can predict at which voltage the interactions in the double layer are absent. This is when exactly zero charge accumulates at the electrode and, as a result, the ions in the salt solution are not attracted. This is the so-called potential of zero charge. An important quantity for electrochemists, according to Koper.

"We do measurements in very dilute salt solutions," says Ojha, main author of the article. "When you make the concentration low enough, you can expect to find the potential of zero charge at some point. But in our measurements with platinum electrodes, we were never able to reach

that point."

## **Eureka moment**

According to Koper, Ojha had the 'brilliant idea' to lower the concentration of the [salt solution](#) even further, by a factor of ten. No one had ever done that before and it turned out to be a eureka moment, because the potential of zero charge finally showed up. "The fact that we have to go to extremely low concentrations tells us that there are many more ions in the double layer than theory predicts," Koper explains. "There is something going on that causes this amount of ions, but that the theory does not take into account."

## **Possible explanations**

What is going on exactly, the researchers do not know yet, although they do have some clues and ideas. Koper: "The nature of the ion does not matter for the number of ions in the double layer. However, the difference in size between the positively charged ion and the negatively charged ion is important. This is because the smaller ion can get closer to the electrode than the larger ion, which causes asymmetry in the measurements." In addition, Ohja noted that the unknown interaction is sensitive to changes in temperature.

When taking these factors into account, Koper cautiously concludes that the explanation cannot be chemical in nature. The ERC Advanced Grant, which the professor received in April 2021, should start to help fill in the missing piece of the puzzle.

## **Updated textbooks**

Based on Ojha's measurements, the researchers have updated the Gouy-

Chapman theory in such a way that it describes and predicts reality more correctly. Ojha: "We hope that our findings will make it into the next generation of electrochemistry textbooks. People do all kinds of electrochemical measurements on metals and with the updated theory they can improve their understanding of the mechanisms and reactions at these kinds of metals."

**More information:** Kasinath Ojha et al, Double-layer structure of the Pt(111)–aqueous electrolyte interface, *Proceedings of the National Academy of Sciences* (2022). [DOI: 10.1073/pnas.2116016119](https://doi.org/10.1073/pnas.2116016119)

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