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Harvesting chlorine from seawater through electrocatalysis

Bert M. Weckhuysen[1,*]

The production of pharmaceuticals and disinfection goods relies on the availability of chlorine. In a recent *Nature Communications* article, Liu et al. report on the electrosynthesis of chlorine from seawater-like solutions through a stable and selective Ru-based single-atom catalyst with low overpotential.

Chlorine (Cl_2) chemistry is considered to be essential to achieving several of the United Nation's Sustainable Development Goals (SDGs) given that Cl_2 is vital to the production of pharmaceuticals, the disinfection of our homes, and the making of safe drinking water.[1,2] The 2020 global production of Cl_2 was more than 88 million tons.[2] Cl_2 is currently produced, next to NaOH, in an electrochemical conversion process, better known as the chlor-alkali process.[2,3] Each ton of Cl_2 consumes around 2,200–2,600 kWh of electricity, making the chlor-alkali industry one of the largest users of electricity. This indicates that any gain in electron use efficiency in this process could have a large impact.

The chlor-alkali process consists of three reactions, namely the chlorine evolution reaction (CER) at the anode, the hydrogen evolution reaction (HER) at the cathode, and the generation of NaOH in the electrolyte.[3,4] Although hydrogen is currently considered an exhaust gas, it could become a major energy carrier in future energy schemes, thereby competing with water electrolyzers, given that the economic value of Cl_2 is higher than that of oxygen, which is the product at the anode in a water electrolyzer system. In other words, when the chlor-alkali electrolyzer units can be coupled to green electrons—provided by, for example, wind turbines—it could become a crucial future technology for the production of green hydrogen as well as Cl_2. Unfortunately, the anodic CER requires a high reaction energy barrier, spurring research activities all over the world to develop more selective and stable anode materials that can lower the energy consumption of CER.

In a recent *Nature Communications* article,[5] Liu et al. report on the use of a Ru-based single-atom catalyst material for the CER. It turns out that this new material operates with a low overpotential (i.e., −30 mV) and excellent stability and selectivity (e.g., 98% Cl_2 selectivity during 1,000 h of operation at a high current density in a flow cell). It also outperforms a commercial dimensional stable anode (DSA) consisting of RuO_2 and TiO_2 when tested under identical conditions. As a result, the authors developed a promising avenue for the electrosynthesis of Cl_2 from seawater-like solutions. As shown in Figure 1, the new electrocatalyst is a carbon-supported single-atom catalyst (CS-SAC). This material is synthesized through a combined carbonization and impregnation process in which a Ru single-atom moiety (SAM) is anchored onto the surface of oxygen-group-enriched ultrathin metal-organic framework (MOF) nanosheet derivatives (MOFNDs). Single-atom catalysis is a hot field of research and has shown to provide new type of catalysts that show promise in electrocatalytic applications.[6,7]

One of the analytical challenges in the field of single-atom catalysis is to

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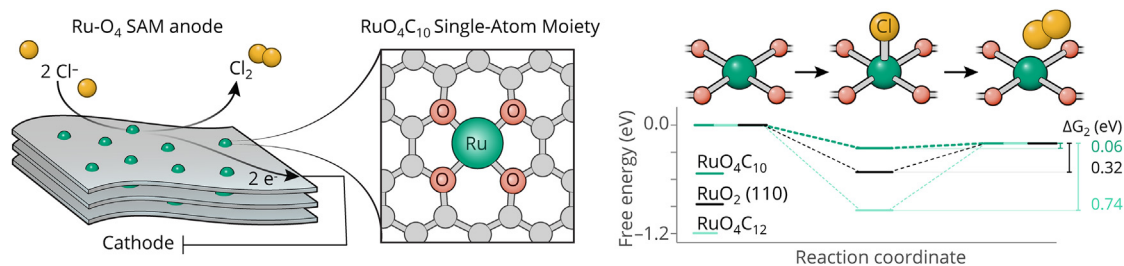
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Figure 1. SAC with a Ru–O₄ moiety (Ru–O₄ SAM) embedded in a MOFND

This material is both very stable and selective in the CER. The combination of theory and advanced spectroscopy experiments shed new insight into the working principles of this catalyst material. This approach points to the existence of the two-step Volmer-Heyrovsky reaction mechanism, in which the experimentally observed Cl* surface species reacts further with a Cl⁻ species near the electrode surface to form Cl_2. The Gibbs free-energy diagram for the second reaction step (i.e., $Cl* + Cl^- \rightarrow Cl_2 + e^- + *$) shows that the RuO_4C_{10} entity has the most balanced Gibbs free-energy change between the first reaction step (i.e., $* + Cl^- \rightarrow Cl* + e^-$) and the second reaction step, enabling easy recombination with another Cl^- in the bulk electrolyte and release from the Ru active center.

unambiguously confirm the single nuclearity of the metal within the catalyst material. For this purpose, Liu et al. used X-ray absorption spectroscopy (XAS) to study the local coordination environment of Ru atoms within the MOFNDs. Extended X-ray absorption fine structure (EXAFS) revealed that there was only one dominant peak at ~1.5 Å caused by the nearest shell coordination of Ru-O bonding, whereas there was no peak at ~2.3 Å, which could be due to Ru–Ru coordination. In addition to hard X-rays, soft X-rays were also used, and the corresponding O and C K-edge X-ray absorption near-edge structure (XANES) revealed a strong chemical interaction between Ru and O on the C substrate, thereby suggesting the formation of C–O–Ru bonds. EXAFS fitting revealed an average coordination number of ~3.8 O atoms around one Ru atom at a distance of 1.99 Å. On the basis of these experimental findings, the authors concluded that the most likely and stable structure is the Ru-O₄ SAM (Figure 1).

To ensure that information on the active moiety and reaction intermediates could be captured during electrocatalysis, the authors expanded their work to *in situ* studies. More specifically, they used *in situ* Raman and infrared (IR) spectroscopy in addition to *in situ* Ru

K-edge XAS. They compared their new material with a reference RuO_2 electrode material. Interestingly, Ru–Cl bonding was observed with Raman on the Ru–O₄ SAM, but not on RuO_2, whereas IR revealed the presence of OCl* species on RuO_2, but not on the Ru–O₄ SAM. *In situ* EXAFS revealed the existence of both Ru–O and Ru–Cl shells but no Ru–Ru shells for the Ru–O₄ SAM, whereas for the RuO_2 material, Ru–O and Ru–Ru features dominated the EXAFS data. Hence, the authors found that Cl can directly adsorb on the Ru sites in the Ru–O₄ SAM during the CER.

In the final step of their work, Liu et al. elucidated the reaction mechanism taking place over the Ru–O₄ SAM material during the CER.[5] For this purpose, they mainly relied on density functional theory (DFT) calculations, where they focused on two possible active-site configurations, namely RuO_4C_{10} and RuO_4C_{12} moieties, which were based on EXAFS fitting and calculated formation energy data. The main conclusions of these efforts are summarized in Figure 1. The authors proposed that the experimentally observed Cl* surface species reacts with a Cl⁻ species near the surface to form Cl_2. The Gibbs free-energy diagram for the CER for reaction step II ($Cl* + Cl^- \rightarrow Cl_2 + e^- + *$) shows that the RuO_4C_{10} entity, in

contrast to the RuO_4C_{12} entity and a reference RuO_2 (110) material, has the most balanced Gibbs free-energy change between reaction step I (* + $Cl^- \rightarrow Cl* + e^-$) and reaction step II, enabling easy recombination with another Cl^- in the bulk electrolyte and release from the Ru active center. In other words, their findings follow the classical Volmer-Heyrovsky mechanism, which is often proposed for other Ru-based CER materials.[4]

The work of Liu et al. clearly shows that Ru-based CER materials made from MOFNDs have the potential to further improve the efficiency of the chlor-alkali process. Although they tested their materials for elongated time periods (>1,000 h), it is clear that real-life conditions are more demanding, and it remains to be seen whether the materials' integrity can be retained during long-term industrial operating conditions. Nevertheless, their detailed characterization work also shows that the careful design and further *in situ* monitoring of an active-site moiety can faciliate the design of new materials, as well as provide further insights into the reaction mechanism of this important process. Surely, their work will lead to follow-up work with the aim of turning the chlor-alkali process into one where both Cl_2 and H_2 can be economically

produced with a minimal loss of green electrons.

DECLARATION OF INTERESTS

The author declares no competing interests.

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Can proteins be used to stop a bullet?

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The answer is now yes! In a just-published paper, Doolan, Goult, Hiscock, and co-workers show that the mechanosensitive protein talin, our cells' natural shock absorber, can be engineered to create talin shock-absorbing materials (TSAMs), hydrogels that are able to absorb the impact of projectiles fired at supersonic speeds. This milestone was achieved using an interdisciplinary approach that combines synthetic biology, chemistry, astrophysics, and materials science and harnesses millions of years of evolutionary optimization that enables mammalian cells to be protected from environmental forces.

Shock-absorbing materials have a multitude of uses across many global industries. They are used to create body armor, protecting the wearer from blasts or projectiles, and are critical to the aerospace industry to protect high-flying airplanes and spacecraft from, e.g., space debris. However, when someone says to you, "Name a shock absorbing material," what you probably don't think to name is a hydrogel, made from the proteins that have been found in all mammalian cells. Doolan et al.[1] have now done just that. They used one of nature's natural protein shock absorbers, the protein talin,[2] to produce a next-generation synthetic biology (SynBio) hydrogel that is capable of absorbing and preserving projectiles shot at supersonic speeds of 1.5 km/s.[3] When you consider that a bullet leaves a gun at between ~0.4 and 1.0 km/s,[4] the fact that this talin shock-absorbing material (TSAM) is so effective is simply remarkable; it could emerge as a viable alternative to current industrial-standard materials.

Talin is a protein found in all animal cells. It is the essential linker that couples the integrin family of extracellular matrix receptors to the cells' force generation machinery.[5,6] This protein contains 13 units (rod domains) that unfold when exposed to force, absorbing this energy while simultaneously introducing slack into the material system.[7] Upon removal of this force, these protein units refold back to the resting state. It is this well-characterized molecular-level property that is retained within the TSAM. Specifically, the first three of talin's 13 shock absorbing rod domains were engineered to produce a monomeric unit with terminal cystine residues. The thiol residue contained in these amino acid residues was then reacted with a synthetic tripodal maleimide cross-linker to produce a polymer that self-assembles into fibers, trapping the aqueous solution. The net result is the TSAM hydrogel, which is illustrated in Figure 1.

The material properties of the TSAM were confirmed by rheology, specifically repetitive and consecutive oscillatory amplitude sweeps. Meanwhile, the presence of hydrogel fibers within the material was confirmed through both scanning electron microscopy (SEM) and fluorescence/transmitted light microscopy. To confirm the shock-absorbing properties of the TSAM in

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