

## Previews

## Mechanistic insights in electro-synthesis of biomass-derived chemicals: The Kolbe reaction

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**Green electrons can be used in the synthesis of biomass-derived chemicals. In this issue of *Chem Catalysis*, Chan and co-workers provide new insights into the Kolbe reaction, which electrocatalytically produces alkanes from carboxylic acids, such as acetic acid. They resolve a debate regarding the origin of an inflection zone in the current-potential curve.**

Combating global climate change is probably one of the greatest challenges our society is facing during this century. If we want to lower the rising CO<sub>2</sub> levels in the atmosphere, we have to develop greener and more sustainable processes for manufacturing our daily goods, including fuels, chemicals, and materials. An attractive option toward a more sustainable society is using green electrons to carry out chemical reactions. This strategy is nowadays coined the “electrification of the chemical industry.”<sup>1</sup> It is defined as using electricity to drive such chemical processes as conversion, heating, separation, and purification and providing the necessary materials and related utilities to assist in operating and controlling chemical processes. When such an ambitious approach is combined with the direct use of agricultural and municipal waste as a carbon source, a fully circular society becomes one step closer. **Figure 1** shows a schematic of a potential synergy between a biorefinery and an e-refinery, in which biomass-derived fuels and chemicals are synthesized with the help of green electrons. In particular, the non-edible fraction of biomass is an attractive starting material for use in combination with renewable electricity.

One of the major hurdles in using biomass as a carbon source instead of,

e.g., crude oil, is the lowering of the oxygen content of biomass-derived oxygenates, such as sugars, sugar alcohols, and fatty acids. These so-called deoxygenation processes require external hydrogen, which comes at an additional cost. This cost is often quite substantial because hydrogen has to be made via, e.g., methane-reforming processes. Researchers are therefore searching for alternative ways to obtain renewable hydrogen. This could become possible if green electrons, which originate from wind turbines, tidal waves, and solar panels, are used in electrolyzers to produce hydrogen and oxygen from water splitting (**Figure 1**, part 5). However, one could also opt to directly use this renewable electricity to perform electro-synthesis reactions on biomass-derived compounds, thereby producing so-called electro-chemicals (**Figure 1**, parts 6–8). The principle of the electro-synthesis of biomass-derived chemicals is presented in **Figure 1** parts 1–4. Although many examples involving, e.g., furan derivatives, levulinic acid, and glycerol exist in recent literature,<sup>3,4</sup> this research topic was already important in the early 1900s, as exemplified by the work of Julius Tafel, who is known for the Tafel equation and rearrangement.<sup>5</sup> The advantage of this approach is that not only can the oxygen content of biomass-derived compounds be lowered, but

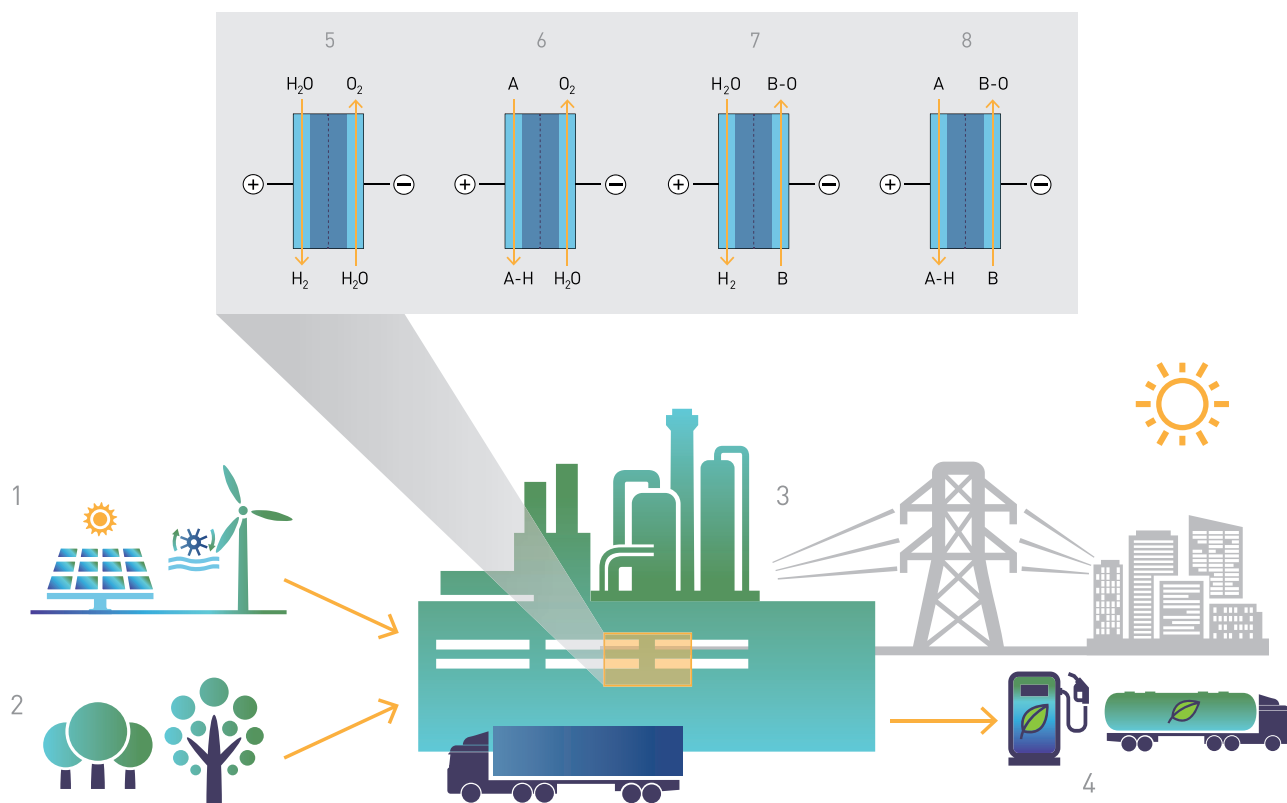
the carbon chain length of the generated organic molecules can also often be increased, thereby providing opportunities to make interesting long-chain hydrocarbons (e.g., liquid fuels) (**Figure 1**, part 4). Schafer has summarized, among others, C–C bond formation for coupling and cross-coupling of, e.g., alkyl-substituted aromatic hydrocarbons to diphenyls and diphenylmethanes at the electrode anion, thereby proposing radical cations as reaction intermediates.<sup>6</sup>

The electro-synthesis process to make C–C coupling reactions possible is named after Hermann Kolbe, who identified in the mid-1800s ethane and octane as the main reaction products of the electrolysis of acetic acid and valeric acid, respectively.<sup>7</sup> Pt, Ir, and Ru are known to be active for this electrolysis reaction. Since its discovery, a lot of research has been performed with the aim of shedding mechanistic light on the Kolbe electro-synthesis process.<sup>2</sup> The main competing reaction during Kolbe electro-synthesis is the oxygen evolution reaction (OER), although its relative contribution clearly depends on the reaction conditions, including the electrode potential. Both competing electrolysis processes taking place are visualized in **Figure 1** parts 5 and 7. A particular feature is the existence of an inflection zone in the current-potential curves, which is ascribed to the transition from the predominance of the production of oxygen (i.e., OER) at lower potential to the production of ethane (i.e., Kolbe reaction) at higher potential, when acetic acid is used as the starting molecule. Furthermore, it has been noted that the OER

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**Figure 1. Principle of the electro-synthesis of biomass-derived fuels and chemicals**

Green electricity produced by, e.g., solar panels, tidal waves, and wind turbines (1), is combined in an electro-synthetic device to make various forms of biomass (2). This can be accomplished in a new generation of biorefineries (3), leading to the synthesis of bio-based fuels, chemicals, and materials (4). Different working principles (5–8) can be applied for the electro-catalytical production of hydrogen and oxygen from water at the cathode and anode, respectively; these processes are called the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) (5), which electrochemically reduce oxygenates at the anode with the production of oxygen from water at the cathode (6), oxidize biomass-derived hydrocarbons at the cathode with the production of hydrogen from water at the anode (7), or in the most advanced mode of operation, use green electricity to simultaneously reduce biomass-derived oxygenates at the anode and oxidize biomass-derived hydrocarbons at the cathode (8). In all of these alternative electro-synthetic processes (6–8), there is direct competition with the HER and OER. This also applies to the Kolbe reaction, which is the topic of Chan and co-workers' recent work.<sup>2</sup>

can be suppressed under anhydrous conditions.

Although initial studies proposed that the Kolbe reaction involves free radicals, it is now generally accepted that electrode surfaces of noble metals promote the reaction rate, so it does not (only) involve a homogeneous solution-phase process. On the other hand, details on why the rate-determining steps of both the Kolbe reaction and OER change as the potential increases (leading to the observed inflection point in the current-potential curves) are still unclear. In this issue of *Chem Catalysis*, Chan and co-workers

use density functional theory in combination with microkinetic modeling to study the reaction mechanism of the Kolbe reaction of acetic acid on both pristine and partially oxidized Pt anodes.<sup>2</sup> Their work provides a framework of thinking that resolves the main mechanistic controversies of the Kolbe reaction, namely the origin of the inflection zone and the identity of the rate-limiting steps. It also provides some practical guidelines for suppressing the OER while aiming for C–C coupling of organic acids.

For the surfaces of Pt(111) and Pt(111)@PtO<sub>2</sub>, Chan and co-workers calcu-

lated the free-energy diagrams for the Kolbe electrolysis of acetic acid and the competing OER of water and developed a microkinetic model, including a sensitivity analysis.<sup>2</sup> They found that the Kolbe reaction efficiently proceeded on Pt(111)@PtO<sub>2</sub> but not on bare Pt(111) in aqueous media at high anode potentials. This observation can be explained by the high barriers for C–C bond breaking of CH<sub>3</sub>COO\* on Pt(111), whose surface is therefore fully covered with CH<sub>3</sub>COO\* species. When comparing theoretical calculations with experimental activity values, the authors found that the Kolbe reaction was limited by the energy barrier

for  $\text{CH}_3^*$  coupling, as well as by the surface coverage of the  $\text{CH}_3\text{COO}^*$  species.

On the basis of their theoretical studies, Chan and co-workers were able to revisit previous theories on the reaction mechanism of Kolbe electro-synthesis.<sup>2</sup> They found that the Kolbe reaction involves adsorbed species, i.e.,  $\text{CH}_3\text{COO}^*$  and  $\text{CH}_3^*$ , thereby excluding the free-radical mechanism, as well as other homogeneous solution-phase processes, from dominating the overall synthesis process. Furthermore, the rate-determining step of the OER on a Pt oxide surface changes from the  $\text{OH}^*$  formation (before the occurrence of the inflection zone) at a low anode potential to  $\text{H}_2\text{O}$  adsorption (during the inflection zone), leading to a passivated OER activity (after the occurrence of the inflection zone) at a high anode potential. At such high anode potentials, a film of Kolbe surface species is formed, thereby blocking the OER from occurring, whereas the Kolbe reaction is determined not by the deprotonation or discharge of acetic acid but by the  $\text{CH}_3^*$  dimerization and  $\text{CH}_3\text{COO}^*$  decarboxylation steps, the latter of which dominates after the occurrence of the inflection zone.

From a more general perspective, the article by Chan and co-workers<sup>2</sup> shows the clear need for a more profound understanding of the reaction mechanism of electrocatalytic processes, especially under realistic reaction conditions. Here, analytical techniques such as vibrational spectroscopy (attenuated total reflection-infrared spectroscopy and surface-enhanced Raman spectroscopy) and X-ray absorption and diffraction could further show their strength. When fully corroborated by advanced theoretical studies, as shown by Chan and co-workers,<sup>2</sup> this experiment-theory approach could show its

full merits. As a side note, the electrochemical conversions of the larger, more organic-type molecules are much more rewarding from a pure spectroscopical point of view than those of small molecules, such as  $\text{CO}_2$ , methanol, and formic acid.

Finally, it is important to remember that Kolbe electrolysis is just one example of an electrocatalytic system that requires more mechanistic insights before the green electrons used can be fully energy efficient. This will become especially true as we move closer and closer to an electrified chemical industry where paired electrolysis schemes, as depicted in Figure 1 part 8, are implemented. Paired electrolysis of biomass-derived compounds, as summarized in some recent review articles,<sup>8,9</sup> could provide interesting leads toward the simultaneous upgrade of a wide variety of biomass-derived compounds. A prototypical example is the electrocatalytic hydrogenation and oxidation of 5-(hydroxymethyl)furfural (HMF) into 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-furandicarboxylic acid (FDCA).<sup>10</sup> Making the two half-reactions compatible with each other and striving for an electron efficiency of 200% will further inspire the careful tuning of solvent properties (e.g., media other than water to avoid competing hydrogen and oxygen evolution reactions) and electrode potentials to maximize the yields of the products formed. By taking Kolbe electrolysis and its competing OER as a showcase, Chan and co-workers<sup>2</sup> have provided us with new inspiration for how such complex reaction schemes could be researched in detail.

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## DECLARATION OF INTERESTS

The author declares no competing interests.

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