Integrating catalysis and new electrolyte concepts into organic electrosynthesis

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Organic electrosynthesis is frequently referred to as an intrinsically sustainable, safe and efficient method [1]. The methodology indeed offers the opportunity to address most of the 12 principles of green chemistry, such as optimizing atom economy, lowering energy consumption, or developing less hazardous syntheses [2]. For example, dangerous and expensive redox agents can be avoided by using electric current, thereby improving atom economy and reducing waste generation as well as energy consumption [3]. Through the electrode potential as the continuously variable driving force, reactions can be carried out under mild conditions, leading to reactive intermediates that are not (or hardly) accessible by conventional means [2,3]. However, implying inherent greenness and efficiency is problematic, since the performance of organic electrosyntheses depends very much on how the method is used.

On the way to efficient and truly sustainable processes, usually several challenges have first to be addressed [4]. These challenges comprise the necessity for employing large amounts of supporting electrolyte additives along with the concomitant separation and waste issues [2,3]. A further challenge is the heterogeneous electron exchange, which is often kinetically inhibited ('overpotential') and coupled to unselective follow-up reactions [5]. A problem that has so far received little attention arises from the frequent use of toxic and environmentally harmful solvents. Owing to their excellent electrochemical properties, DMF, acetonitrile, HFIP, or other harmful candidates are often used in academic research, rendering a transfer to a technical scale difficult.

The present contribution deals with catalytic approaches and electrolyte concepts that are designed to overcome abovementioned challenges. For illustration of the principles, 'classics' and recent cases from our research are used. These examples include applications of homogeneous electrocatalysis [6], multifunctional electrolyte systems [7], and studies into 'green' solvents and salt additives [8].

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