Concluding Remarks: A Faraday Discussion on Electrosynthesis. A Summary of Discovery and Opportunity

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A Summary of the Faraday Discussion on Electrosynthesis.

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A summary of the Faraday Discussion presented in this Special Issue and a perspective on that discussion is presented. The work highlights the specific science contributions made and the key conclusions associated with those findngs so that readers can identify papers that they would like to explore in more detail.

Introduction

Electrochemistry offers an opportunity to conduct oxidation and reduction reactions under neutral conditions, trigger interesting new umpolung reactions, and recycle chemical reagents so that they can be used in catalytic amounts.[1] Yet in spite of these opportunities and impressive advances in electrosynthetic techniques by individuals in the energy conversion community, for many years the larger synthetic community mostly ignored electrochemistry and viewed it as a highly specialized, niche technique. During this time, broader applications of electrosynthesis were mainly studied by a small, dedicated group of scientists who worked to better understand the key elements of electrochemical experiments, to determine how electrosynthetic reactions could be optimized and developed, and to provide examples of how electrochemistry could be utilized in more complex settings. The hope was that this effort would illustrate for the larger synthetic chemistry community the potential of electrochemical methods so that they might be tempted to capitalize on the approach in their own work. This effort was not undertaken in vain, and today a rapidly growing number of synthetic chemists are exploring and taking advantage of electrochemistry. This influx of new people, talent, and ideas is driving the development of electrochemical methods in ways far beyond what the original practitioners of the field could have ever imagined. Today, it is an exciting time to take stock of what we have been learning and to think about what new opportunities lie ahead in the future. It was in this light that the Faraday Discussion on Electrosynthesis was held.

The discussion opened with remarks by Professor Toshio Fuchigami (Professor Emeritus, Tokyo Institute of Technology and Director, Sagami Chemical Research Center).[2] Fuchigami outlined the history of electrochemistry over his career highlighting direct and indirect electrochemical reactions, the

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development of new electrochemical mediators, and the use of electroauxiliaries, ionic liquids as solvents, modified electrodes, conducting polymer films, thin layer flow cells, new electrode materials, recyclable hypervalent iodide oxidants, solid phase electrodes, paired electrolyses, bipolar electrodes, N-centered radicals, and selective fluorination reactions. The review illustrated how these methods (with many contributions from the Fuchigami group) laid a foundation for much of the electrosynthetic chemistry

Professor Toshio Fuchigami

being pioneered today. This historical perspective told a "story" of what electrochemistry was capable of and how we might achieve it.

This electrochemical "story" is still being developed qith much of the current push occurring along two main, very broad themes. First, a large effort is underway to discover the new synthetic capabilities that electrochemical methods make available; capabilities that increase our ability to build (or detect) molecules in ever more efficient and selective ways. Second, significant effort is being put into the development and application of electrochemical approaches to meet societal needs in more sustainable ways. The Faraday Discussion addressed work that fit into both of these themes with an emphasis on providing the new mechanistic insights needed to drive innovation. What follows is a summary of those discussions that is meant to point readers to original papers in the issue, papers that address topics they are interested in exploring in greater detail.

Results and Discussion

The main body of the meeting commenced with an intriguing paper by Alexander Kuhn and co-workers that describes the use of a magnetic field to propel designed particles through solution.[3] The particles, comprised of a Zn-core coated with a chiral oligomer, mediate the reduction of ketones to chiral alcohols with high enantioselectivity (Scheme 1). Movement of the particles through solution in the presence of the magnetic field aids convection on the surface of the particle in a way that raises the efficiency of the chiral reduction reactions by an order of magnitude. It is a method that offers a unique approach to minimizing the mass transport properties that can impede the use of heterogeneous catalysts. The group discussion of the paper focused on how the particles, or "swimmers", were propelled through solution, the nature of the oligomers on the surface of the particles, the scope of the reactions that might be possible including potential oxidation reactions, and the chemistry that was happening on the Zn-terminus of the particle. The discussion was driven by a desire to understand more deeply how the chemistry worked with an eye toward how the "swimmers" could be applied in future synthetic efforts.
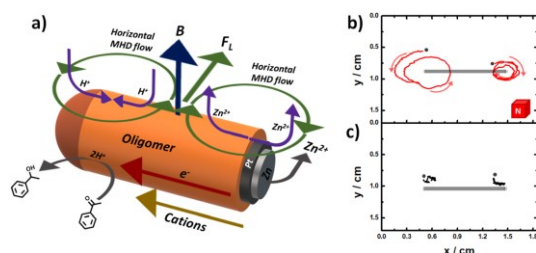
Scheme 1. The use of magnetic fields to propel Janis-swimmers through solution. Image taken from reference 3.

The next paper in the session also focused on using technological advances to forward an electron transfer process. In this case, Long Luo and his group discussed how controlling the frequency of an alternating current reaction can alter the selectivity of H/D- (or H/T-) exchange reactions involving tertiary amine substrates (Scheme 2). When the reactions were performed using current state-of-the-art methods, they are typically non-selective and lead to total exchange of all relevant hydrogens.[4] The talk detailed a mechanistic picture of the desired reaction pathway (oxidation of the amine followed by deprotonation to form a radical that then abstracts a deuterium from a deuterated thiol) and highlighted its rate relative to a pair of potential side reactions (dimerization of the initial formed radical intermediate and over-oxidation). The data presented then showed how that understanding could be used to select either the use of a direct or an alternating current electrolysis for the transformation. For the two substrates highlighted here, very different reaction conditions were needed to accomplish the desired outcome. For the functionalization of **1**, the use of a direct current proved to be the method of choice due to an underlying dimerization reaction that interfered with the alternating current reactions.

For the functionalization of **2** the subsequent D-atom abstraction reaction was fast leading to a reaction that
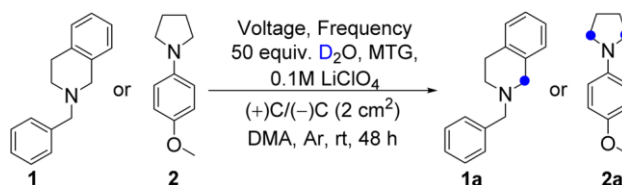
Scheme 2. H/D-exchange using direct or alternating current electrolyses. Image taken from reference 4.

benefited from the use of an alternating current. The discussion of the paper focused on how these conclusions were reached, how the selectivity of the reactions was obtained for the processes, and what other examples could be used to illustrate the true power of the method for inducing selectivity into chemical transformations.

Toshiki Nokami and coworkers then presented their use of electrosynthesis for the automated synthesis of complex cyclic dodecasaccharides (Scheme 3).[5] Automated syntheses require a method that is consistent, reproducible, and flexible enough to handle changes in the structure of various substrates. In this case, a constant current electrolysis of anomeric thioethers provided just such a method. The constant current electrolysis allowed for the potential at the anode to adjust to both changes in potential caused by variations in the large substrates employed and the use of a second thioether with a higher potential as a part of a dimerization-cyclization sequence. In the dimerization-cyclization sequence, oxidation of a thioether with a lower potential was used to generate the reactive species needed for the dimerization step while oxidation of a thioether with the higher potential allowed for the cyclization. The discussion of the paper following the presentation focused on the coupling steps, the intermediates involved, and the role that the electrolyte in the reaction played in that process. There was a general agreement that the ability to do the anodic oxidation on molecules of the size employed was truly impressive in terms of the mass transport issues that frequently hinder heterogeneous reactions with larger substrates.
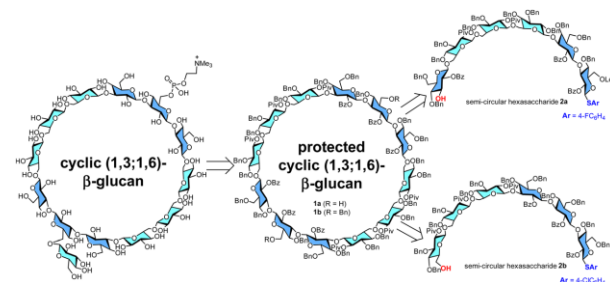
Scheme 3. An automated route to macrocyclic sugar natural products. Image taken from reference 5.

Next up was an intriguing paper by Julia Stuwe and Lutz Ackerman that describes a systematic study of 21 different photocatalysts for use in the photoelectrocatalyzed CH-trifluoromethylation of arenes (Scheme 4).[6] As is often the case,

the use of photoelectrochemistry was necessary for the reactions because it allowed access to high oxidation potentials without the need for high electrode potentials. In the science presented, it was found that two metal free catalysts ([Mes-Acr]ClO$_4$ and [TAC]ClO$_4$) were optimal for accomplishing the desired transformations. The catalyst, light, and current were all required for generation of the trifluoromethyl radical. The study provided an excellent example of how a constant current electrolysis can allow for a systematic study by adjusting to the various oxidation potentials of the catalysts without a need to change reaction conditions. Discussion of the paper by attendees at the meeting focused on mechanistic questions having to do with the light source, and how the reactions led to improved yields relative to non-electrochemical methods while still producing the products with similar selectivities. For most cases, the two optimal catalysts behaved similarly, but for a more complex example associated with a natural product synthesis the [TAC]ClO$_4$ was a superior choice. At this time, it is not clear why one catalyst was better than the other one in these cases; an observation that highlights the need to screen
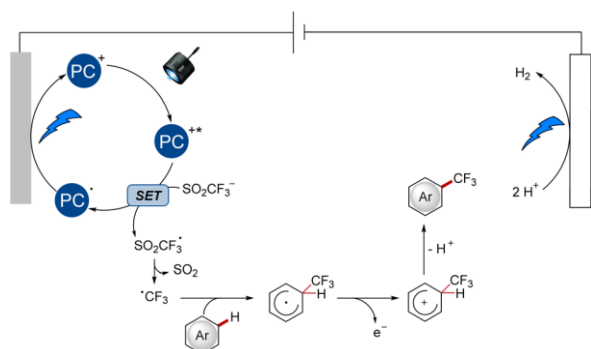

Scheme 4. A photoelectrocatalytic method for the trifluormethylation of arenes. Image taken from reference 6.

catalysts for a given reaction.

The use of pyruvate as an electrolyte was shown by Chase Bruggeman, Karissa Gregurash, and David P. Hickey to afford significant advantages for the electrochemical reduction of NAD$^+$-biomimetics (Scheme 5).[7] Typically, the reduction of NAD$^+$-biomimetics is complicated by dimerization of the radical intermediate generated, a radical that is supposed to undergo a second reduction and then protonation step. The authors screened a number of additives/electrolytes to prevent the dimerization and found that one of them, sodium pyruvate, was effective, led to significant yields of the desired NADH mimic, and afforded far lower yields of the unwanted dimer. Methyl pyruvate was also compatible with suppression of dimer formation. The discussion of the paper focused on the reason for this observation, and during that discussion a proposed mechanism where the NAD-radical was stabilized by a reversible electron transfer to the pyruvate was suggested. Alterations to electrode material and other reaction conditions were discussed, and the authors pointed out that these changes did not influence the reaction to a great extent. The paper and the discussion that followed reflected a general theme of many

of the discussions that followed, a theme that focused on how electrolytes, counter-ions, and additives influence the reactive intermediates and products generated by the electrochemical transformation.
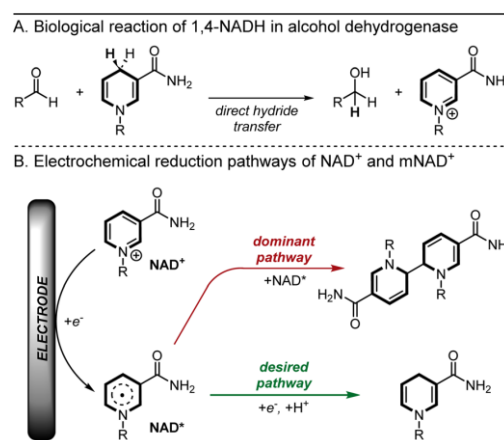
Scheme 5. The use of pyruvate to channel NAD$^+$-mimic reduction toward the desired NADH-derivatives. Image taken from reference 7.

Victoria Flexer, along with Walter R. Torres and Nadia C. Zeballosa, then presented their efforts to demonstrate how lithium ions could be isolated as lithium carbonate from brines comprised of mixed cationic species (Scheme 6).[8] The project fits into a larger societal-need to isolate lithium without resorting to large evaporation pools that frequently throw away water in arid regions. The approach works by taking advantage of a membrane electrolysis where cations in the brine solutions are transported from an anodic chamber to the cathodic chamber. Ca- and Mg-ions are transported across the membranes more rapidly than Li-ions facilitating their removal from the original brine solution. The amount of sodium present in the resulting mixture can then be reduced by the precipitation of sodium bicarbonate at the correct pH. Following this pre-treatment, the remaining Li-, Na-, and K-cations are pushed across a new membrane to a cathodic chamber where carbon dioxide is being reduced to form
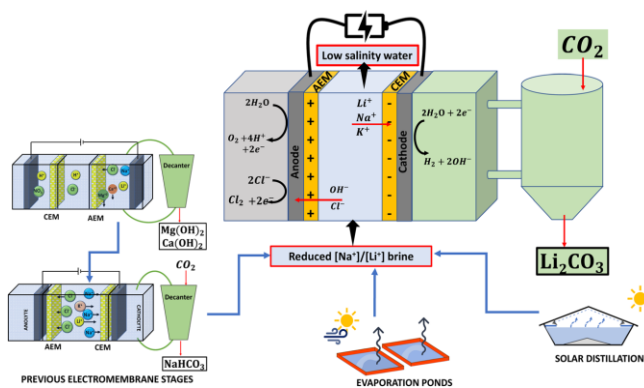
Scheme 6. A membrane electrolysis approach for the isolation of lithium carbonate from brine mixtures. Image taken from reference 8.

carbonate. With proper pH control in this cathodic chamber selectively precipitation of $LiCO_3$ from the solution can be achieved. The discussion of this paper focused on technical details of the membranes used, the scale of the process that can be conducted, and how the process might be merged with other efforts to remove heavy metals in order to reduce its overall environmental impact.

At this point, T. Leo Liu and his group discussed mechanistic efforts to understand how the biaryl byproducts that frequently complicate Ni-mediated cross coupling reactions are formed (Scheme 7).[9] The work indicated that the rate limiting step for the reaction is the oxidative addition of a cathode derived Ni(I)-species to an aryl halide. This step is followed by the reductive generation of a Ni(II)-species by Ni(I) in solution that in turn triggers a ligand transfer where an aryl-group on the Ni(II)-species is transferred to a second Ni(III)-species generated from the initial oxidative addition. The result is the formation of a bis-aryl Ni(III)-species that undergoes reductive elimination to form the undesired biaryl byproduct. The identification of the Ni(II)-species led to the development of a new method to trap it with a benzylic radical leading to a different cross coupling reaction, and the identification of approaches to avoid biaryl formation in the initially planned cross coupling reactions. The discussion that followed the presentation focused on a number of technical questions about the generation of the Ni(II)-species, its possible generation at the anode, and the role electrolytes might play in the process. What was abundantly clear from the paper and the discussion that followed was how mechanistic insight about the process was being used to develop new synthetic protocols.
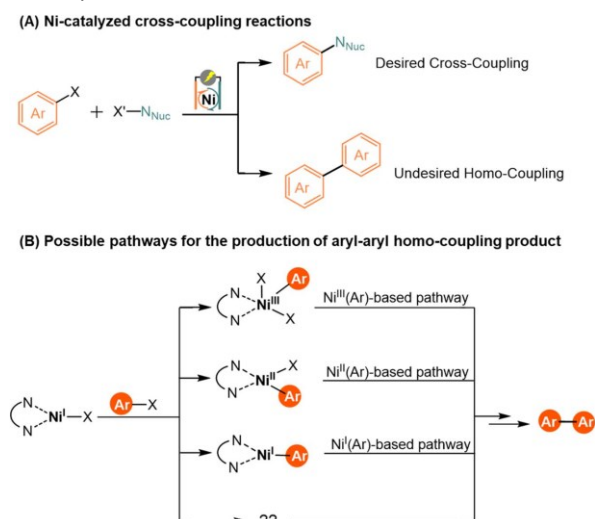
Scheme 7. A mechanistic study on the origin of biaryl products in Ni-mediated cross coupling reactions. Image taken from reference 9.

Work presented by Dylan G.Boucher, Zachary A. Nguyen, and Shelley D. Minteer then showed that a similar mechanism operated in Co- and Fe-based systems and illustrated the role electrolyte can play in mediating such processes.[10] Shown in Scheme 8 is the mechanistic paradigm presented for these reactions. In this case, an initial reduction afforded a Co(I)-

species that then underwent the oxidative addition step to form a Co(III)-intermediate. The Co(III)-intermediate was reduced to a Co(II)-intermediate that then had the potential to transfer an anion. However, the anion was not automatically transferred. In this example the authors found that the fate of the Co(II)-intermediate was determined by the electrolyte used. When a electolytes with softer cations were used, the Co(II)-complex was stable and Reaction 4 in Scheme 8 did not readily occur to produce the anion. When electrolytes with harder cations were used, dissociation of the Co(II)-complex to form the anion (R- in Scheme 8) was favoured. Similar observations were made for the analogous iron-mediated chemistry. The discussion that followed focused on the role of ion pairing in the electrolyte solution and questions concerning the overall solvation of the anions and organometallic species present. The general consensus was that the systems defied a single simple explanation, and that work to gain a better understanding of electrolyte/intermediate interactions was essential for the design of future reactions.
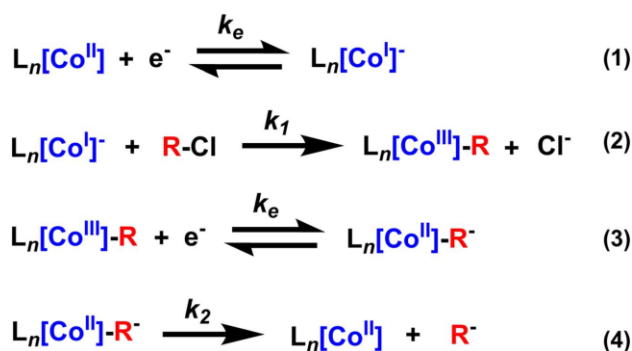
Scheme 8. The influence of electrolyte on Co- and Fe-mediated reduction reactions. Image taken from Reference 10.

A similar electrolyte dependence was observed by Bernardo Frontana-Uribe and his group.[11] In their paper highlighting the utility of biomass derived dihydrolevoglucosenone (Cyrene™) as a new environmentally compatible solvent, they observed that the reduction of diphenyl ketone derivatives afforded different products when tetrabutyl ammonium tetrafluoroborate was used as the electrolye relative to reactions where $LiClO_4$ was used as the electrolyte (Scheme 9). For starters, dihydrolevoglucosenone did prove to be an effective solvent for both reactions. It has a polarity similar to dimethylformamide or acetonitrile, although the reactions did require the use of ethanol as a cosolvent because of its viscosity. The discussion of the paper focused on the solvent in terms of its stability to acid or nucleophiles (not an issue to this point), the possibility that the use of dihydrolevogulcosenone as solvent might induce enantioselectivity into a reaction (currently the solvent has influenced the diastereoselectivity of reactions but no evidence of enantioselectivity), the overall conductivity of the system studied, and the how the electrolyte altered the selectivity in the reactions presented. With respect to the electrolyte, the discussion again focused on the ability of the cations to complex the alkoxides being formed with the use
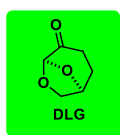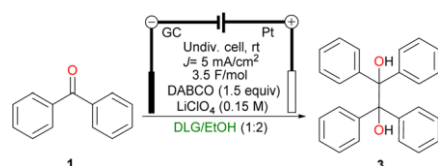
of lithium leading to complexation of the alkoxide and optimization of the radical character of the intermediates generated. This favoured the dimerization pathway.

Of course, the electrodes used in an electrolysis can also play

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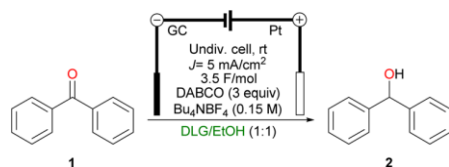
b)

Scheme 9. The use of dihydrolevoglucosenone as an environmentally benign solvent and the role of electrolytes in product determination. Image taken from reference 11.

a large role in determining the outcome of the reaction. Yun-Ju Liao, Shih-Ching Huang, and Chia-Yu Lin presented a paper that discussed the use of modified electrodes for the conversion of biomass into synthetic building blocks for materials science applications (Scheme 10).[12] The worked focused on ITO electrodes that were coated with a nano-NiOOH borate film. The films were applied to the ITO electrodes by electrodeposition. The authors showed how the quality of subsequent alcohol oxidation reactions at the electerodes depended on the method used for the synthesis of the nano-
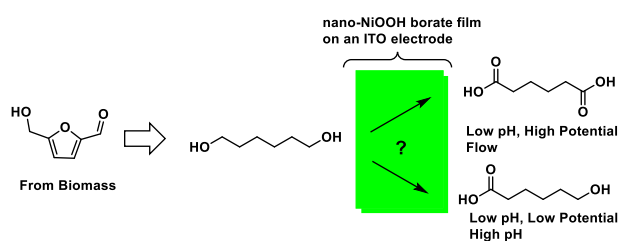
Scheme 10. The use of nano-NiOOH borate films on ITO for the oxidation of biomass derived alcohols.

NiOOH borate film, and then illustrated for the oxidation of 1,6-hexane diol that either adipic acid could be formed at low pH and high potential in a flow system or 6-hydroxyhexanoic acid could be formed at either low pH at low potentials or at higher

pH's. Reaction optimization afforded a chance to look more carefully at the mechanism of the oxidation pathways.

The focus on electrodes continued with a paper presented by Professor Jeannie Tan and her group (Scheme 11).[13] While the capture of carbon dioxide to form carbon monoxide has been optimized, the conversion of CO into value added products remains problematic. In this paper, the authors point out that the conversion of CO to ethylene is highly dependent on the nature of the cathode material. They explored bimetallic catalysis comprised of a Cu(core)-nanoparticle deposited with either Co, Pd, of Ag on a carbon-GDL base. The Ag-Cu nanoparticle provided the best performance. The discussion that followed focused on optimization of the system, how products were separated, the rationale for choosing the alloys
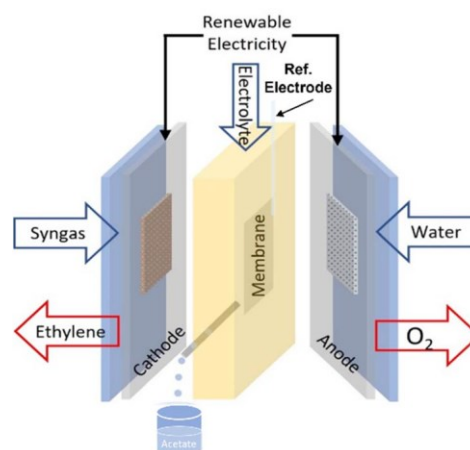
Scheme 11. Optimizing the conversion of CO to ethylene. Image taken from reference 13.

studied, the source of the hydrogen atoms on the ethylene product (syn gas or the water/methanol solvent), and the possibility of labelling studies. Throughout, the discussion focused on how we can think about the process and the role of the electrode in accomplishing the desired transformation.

In another paper focused on the use of functionalized electrodes, Tala Ashraf from the group of Bastian Timo Mei (along with co-workers Ainoa Paradelo Rodriguiz and Guido Mul) described their development of platinum-nanoparticle coated boron doped diamond electrodes and their use for the electrochemical decarboxylation of acetic acid (Scheme 12).[14] The long range goal of the work is the removal of acids from pyrolysis oil, a step that is involved in converting the oil into value added materials. Because of the importance of the reactions, the mechanism of the decarboxylation reaction was studied at a variety of electrodes. The Pt-nanoparticle-coated electrodes improved selectivity for the formation of Kolbe-type products. Boron doped diamond turned out to be the best base electrode material for the experiments because of its high over-potential for oxygen evolution. The reactions led to the formation of methanol as a by-product due to the generation of hydroxyl radicals at the electrode surface. The discussion that followed focused on the what the electrodes looked like following the reaction and how stable the surfaces were with
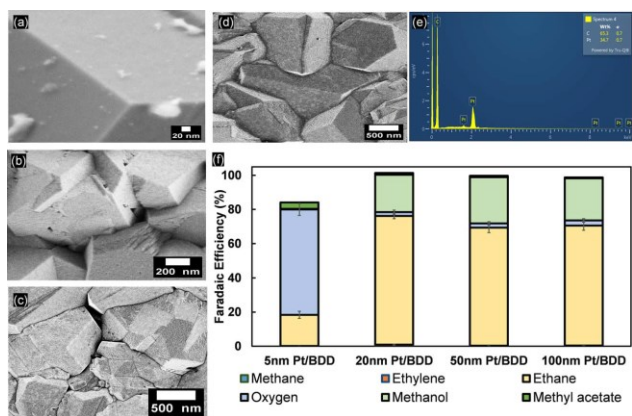
Scheme 12. New electrode materials for decarboxylation reactions. Image taken from reference 14.

respect to changes during the electrolysis, the procedure for how the nanoparticles are made and how the shape of those nanoparticles can be controlled, the spectroscopy of the surfaces, and the generality of the reaction for the production of more complex Kolbe products looking towards the future.

In a paper that built upon a theme of utilizing biomass waste to synthesize products of value, Robert Price and co-workers examined the use of PMA ($H_3[PMo_{12}O_{40}]$) as a M=O-based catalyst to utilize the organic waste being generated from whisky production as a source material for the production of hydrogen gas (Scheme 13).[15] The chemistry involves oxidation of the organic waste stream that in turn reduces the catalyst and loads it with hydrogen atoms. The catalyst is then regenerated by oxidation leading to the release of protons that then pass through a Nafion membrane and get reduced at a cathode to form hydrogen gas. The work examined the nature of the waste stream from whisky production in order to determine at which stage of the process the waste generated would lead to the most efficient electrochemical process for the production of hydrogen. In this study, it was determined that the use of Pot Ale from the second step of the whisky process was the best source material for catalyst loading (about 70% coating of the catalyst) leading to the largest amount of
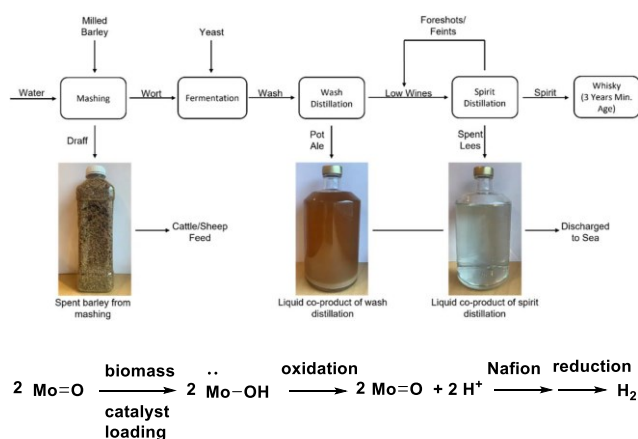
Scheme 13. Studying the utilization of whiskly waste streams for the production of hydrogen. Image taken from reference 15.

hydrogen production. However, it appeared that the use of the Draff waste from the first step could be optimized further for near complete efficiency in the catalyst loading step. The discussion of this paper revolved around the ability to scale the process, the energy efficiency of the overall approach, what could be done with the new waste generated from the loading step, why the choice of the PMA catalyst, and how one might accomplish the reaction catalytically given that the loading step in the process is currently a stoichiometric reaction.

In a manuscript describing the synthesis of catalytically active zirconium-doped manganese oxide nanoribbons, Subin Kaladi Chondath and Mini Mol Menamparambath presented their work on the synthesis of materials at a water/chloroform interface (Scheme 14).[16] The authors pointed out that while electrochemical methods are great for making uniform, pure conducting polymers, they are not always compatible with making those polymers with metal catalysts imbedded in them. For that reason, the authors have used a chemical oxidation to trigger polymerization from an EDOT-monomer at a water/chloroform interface. The interface was used to confine the synthesis to a two-dimensional plane. The result of the chemistry was the synthesis of nanoribbons imbedded with K-OMS-2 structures that are doped with Zr. The Mn-catalysts have the basic MnO_2 structure KMn_8O_{16}. During the discussion of this paper, questions focused on what was next now that the nanoribbons were available (are there applications for the material in electrosynthesis), on what the role of the Zr-complex is during the synthesis since the reaction did not proceed without it, and how scalable the process is.
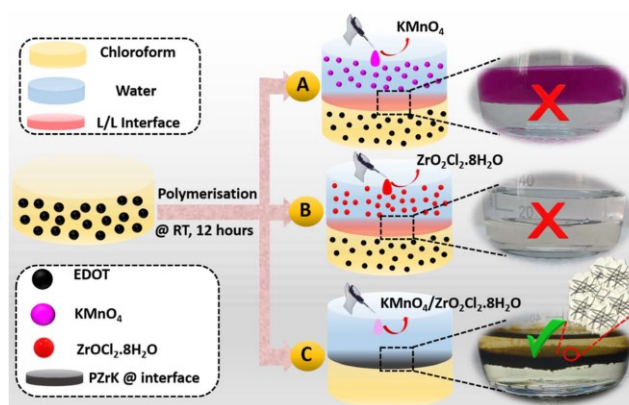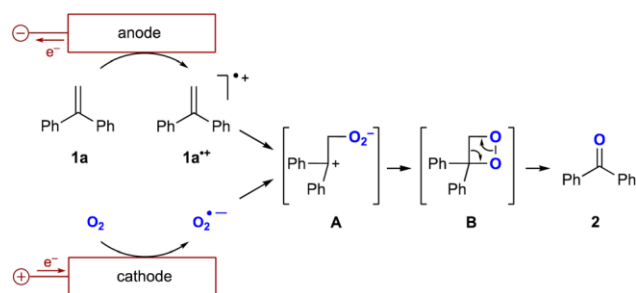

Scheme 14. The synthesis of functionalized nanoribbons on an interface. Image taken from reference 16.

While many of the papers presented during the meeting discussed how mechanistic insights can be used to improve existing electrosynthetic reactions, the consideration of the electrochemical mechanisms can lead to entirely new approaches to synthesis. In their paper, Sevyedamirhossein Hosseini, Joshua A. Beeler, Melanie S. Sanford, and Henry S. White presented a method for conducting oxidation reactions under reductive conditions and reduction reactions under oxidative conditions (Scheme 15).[17] The reactions work by generating reactive intermediates that fragment to afford
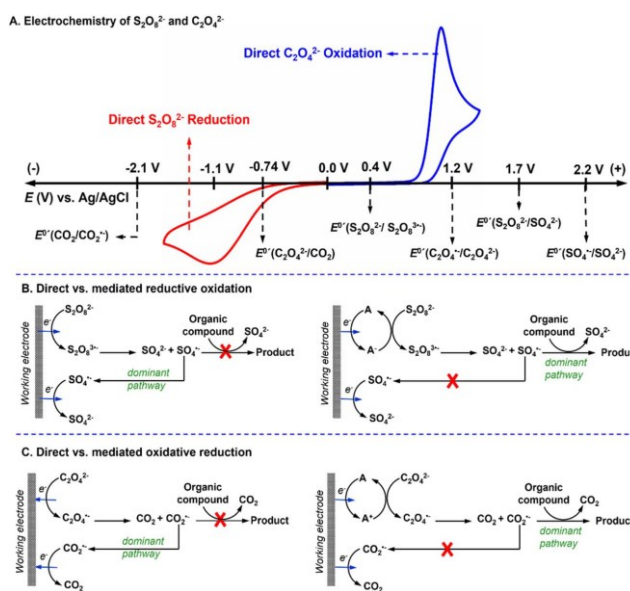
reactive oxidants or reductants. For example, the mediated reduction of $S_2O_8^{2-}$ leads to a radical anion that fragments to form sulfate and sulfate radical anion ($SO_4^{-\cdot}$). The sulfate radical anion is a very strong oxidant. Hence, the original reduction generates a species capable of oxidizing a variety of organic substrates. Because the oxidant is generated at a cathode, it can be produced without worrying about the oxygen evolution reaction, a scenario that opens the door to new types of applications. In the opposite direction, the authors showed how the mediated oxidation of oxylate ($C_2O_4^{2-}$) affords a radical anion that then fragments for form the radical anion of carbon dioxide ($CO_2^{-\cdot}$). This radical anion is a strong reductant that will transfer an electron to organic molecules in order to generate carbon dioxide. In this way, the original oxidation reaction generates a powerful reductant, and again sets up the opportunity to do unique chemistry. The conversation following this presentation focused both on the details of the transfromations and on the opportunities the reactions made available for new functional group compatibility. Professor Richard Brown asked an intriguing question about how one

Scheme 15. Conducting reductive oxidations and oxidative reductions. Image taken from reference 17.

could take advantage of the reactive species migrating away from the electrodes and their interactions with groups that were attracted to the electrode surface since the cathode attracts electron-poor groups. Could the reactions be used to conduct a selective oxidation of an electron poor species attracted to the cathode and in so doing reverse the normal selectivity for an oxidation reaction?

Rojan Ali, Tuhin Patra, and Thomas Wirth discussed how flow electrochemistry can be used to develop practical alternatives to the ozonolysis reaction (Scheme 16).[18] For this transformation, a convergent paired electrochemical strategy is used to combine the product generated by the cathodic reduction of oxygen with the product generated from anodic oxidation of an electron rich olefin.[1q] The radical anion and

radical cation generated undergo an addition reaction that affords a cyclic dioxetane structure that then fragments to a ketone. Key to this reaction is the biphasic (gas/liquid) reaction that illustrates how gases can be utilized in a flow reactor. The biphasic system (employing a segmented solvent approach) led to excellent mixing and facilitated the transformation. The discussion of this paper focused on issues associated with gas diffusion, where the oxygen was reduced, and suggestions for improving gas solubility with a focus on reaction optimization.

Scheme 16. A flow electrochemical method for the cleavage of olefins. Image taken from reference 18.
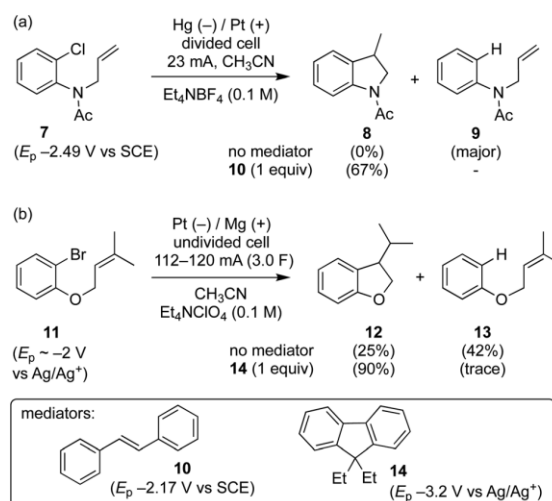
A collaborative project between the groups of Guy Denuault and Richard C. D. Brown discussed the intriguing observation that mediated reduction reaction can work with a mediator that reduces at a more negative potential than the substrate (Scheme 17).[19] The fact that the products generated were indeed a product of a mediated process and not a direct reduction was established by demonstrating that the mediated electrolysis reaction led to a different product than the direct (reaction one in the Scheme), and then showing that the example with the more negative mediator led to the product from the indirect electrolysis (reaction two in the Scheme). The presentation went on to make the point that the normal consideration of potentials ignores mass transport at the electrodes. Using a series of simulations, the authors illustrated


Scheme 17. Mass transport phenomena in mediated electrolyses. Image taken from reference 19.

how at the very start of the reaction both the substrate and the mediator were reduced, but following the initial reduction that consumed the starting material at the cation reduction of the mediator occurred. As that mediator migrated away from the cathode, it encountered unreduced substrate and reduced it in a manner that prevented the substrate from reaching the electrode surface. This left only mediator at the electrode which was reduced, migrated away from the cathode, and again encountered substrate that was migrating toward the electrode. The cycle was repeated leading to formation of the product from the indirect electrolysis. The result of the work is an opportunity to rethink how we design new mediator/reaction systems. The discussion of the manuscript focused on technical questions, rate constants, and an effort to gain a better understanding of how to think about the systems. Professor Fuchigami raised the idea of an alternate method for generation of the cyclization product (typically derived from the mediated process) from a direct reduction reaction using sonication.

Finally, Bria Garcia, Jessica Sampson, Mary P. Watson, and Dipannita Kalyani presented their efforts to compare electrochemical and chemical cross electrophile coupling reactions utilizing primary and secondary alkylpyridinium salts (Scheme 18).[20] The talk presented details of a study that used high-throughput experiments to conduct a systematic comparison of the scope of the aryl bromides that could be utilized with both substrates. It was found that the trends observed for the different arylbromides (with 37 different arylbromides examined) were similar with the use of the two different alkylpyridinium salts. The study included 13 more complex aryl bromides in the library. For most cases, the electrochemical and chemical approaches were similar. The chemistry illustrated a general approach for evaluating the true potential of an electrochemical method in the context of its chemical alternative, a comparison that is essential if we hope to define for a larger synthetic community the true value of the electrochemical methods being developed.
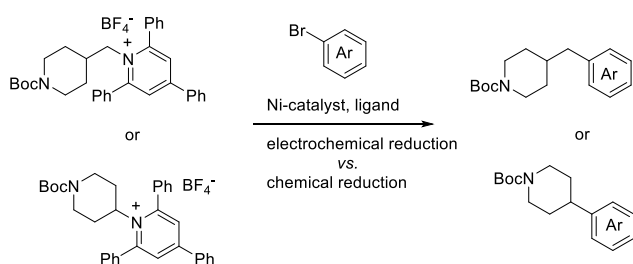
Scheme 18. A comparison of chemical vs. electrochemical Ni-mediated cross electrophile coupling reactions.

Conclusions

New synthetic chemistry is often the product of new mechanistic insight. It is our understanding of how things work that drives innovation, and it was an effort to gain that understanding that drove the discussion during this meeting. In one form or another, the question asked after every single presentation was "how does this work?". Participants sought details that would enable them to best think about the methods discussed and better design their own experiments in the future.

Those discussions led to several themes that were consistently raised. In connection with efforts to develop new synthetic capabilities, questions were asked about how we can more carefully define the role of electrolytes in our reactions and then use those observations as design features in connection with future transformations, how we can capitalize on what we are learning about the design of electrode surfaces and the subsequent control of product selectivity, and how we can translate new, intriguing scientific discoveries like reductive oxidations into new methods that accomplishing things that cannot be done any other way?

In connection with efforts to utilize electrochemistry to make more sustainable processes, the questions asked concerned how we can best balance fundamental studies with providing practical solutions to societal-challenges, and whether the problems we are working on are truly solvable with the fundamental discoveries being made? It was generally understood that it is the answer to these questions that will help define the long-range utility of electrochemistry and how the larger community adopts and takes advantage of those methods in the future.

While the meeting impressively focused on mechanistic details of the methods being developed, at the end of the discussion the synthetic organic chemistry part of me was left with a feeling that we can still do better. On many occasions, we appropriately pointed out how synthetic chemists would benefit from paying more attention to the electrochemical details of the reactions they are running. Participants familiar with electrochemical methods for energy conversion and harnessing available sources of carbon like carbon dioxide know how to think about surface control of reactions, electrocatalysis, and cell optimization in ways that would enrich broader synthetic efforts. But, that information exchange is a two-way street.

When doing electrosynthesis, do we think enough about the physical organic chemistry part of our electrochemical reactions? We talk about the selectivity of kinetically controlled reactions, but how many transition state pictures are included in those discussions even though it is the transition state that determines that selectivity? How many times do we as a community define if a reaction is under thermodynamic or kinetic control, or talk about electrolytes as counter ions for alkoxides in a broader context of what is known about enolates and/or alkoxides in general? How many times is a reaction discussed without a structure or potential mechanism illustrated that would provide a context for that discussion?

These comments are not meant to be a criticism; just an observation and a challenge. As a community, can we get more out of our question "how does this work" if we think about both electrolytes, electrode surfaces, cell design, and the physical organic chemistry behind the reactions we are pursuing? The answer to that question is yes. The "story" of what electrochemistry offers for the larger community is being

defined at impressive pace. By more completely considering both the electrochemistry and the physical organic chemistry elements of that story, we who spend our time at that interface can better define for others how to think about electrochemical events and the reactions they trigger. In so doing, we will make the chemistry accessible to an even greater number of scientists, and it is that expansion of the number of talented people working on electrochemical methods that will truly drive new innovation and a still more expansive future.

Conflicts of interest

"There are no conflicts to declare".

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Notes and references

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