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Hydrogenases – Achievements and Expectations

Biologically important enzymes

The importance of hydrogenases has been recognised by researchers the world over since their discovery in the 1930s. These amazing, biologically important enzymes, which have caught the attention of not only biologists, are able to catalyse the evolution and uptake of hydrogen. Inorganic chemists have also been intrigued by the vital role that these enzymes play, especially as hydrogenases have an organometallic (iron–carbonyl) active site, and have, over the years, synthesised and probed countless models that mimic these enzymes with the hope of elucidating, among other things, structure–activity relationships. They have also studied and characterised both the enzymes and their models by a multitude of techniques, always striving to understand the mechanisms by which these enzymes function. The ever-pressing need to find renewable energy-sources has made these researchers look even more closely to hydrogenases, because of their catalytic production of hydrogen.

Potential for renewable energy sources

EurJIC also acknowledges the value of hydrogenases, and it is therefore with great enthusiasm that we, with our Guest Editors for this issue, Marcetta Darensbourg and Wolfgang Weigand, offer you a cluster issue on hydrogenases. In this

Guest Editors Marcetta Darensbourg Wolfgang Weigand

issue, we are proud to have leading international experts at the forefront of hydrogenase research showcasing their achievements. Topics surrounding all three classes of hydrogenases, the [FeFe]-, [NiFe]- and [Fe] hydrogenases, are featured. It is always good to have a mix of articles to catch the attention of our wide audience, and I am delighted that we are able to achieve that as can be seen from the great selection of peer-reviewed papers that touch on biosynthesis, structure, mechanism and application.

As the opening paper of this issue we are pleased to present an Essay. It is not usual for *EurJIC* to publish essay-type articles; however, we believe that an overview of the topic of a cluster issue, given by a distinguished, well-respected figure in the field, can only be considered as the cherry on the top! We are glad that Rolf Thauer agreed to be the author of the essay; in it, he offers his reflections on the hydrogenases and the global H₂ cycle. Of the twenty-six articles, we have eight Microreviews and three Short Communications. It is not common practice, once again, for *EurJIC* to have as many reviews in a single issue, but, as you will see, each emphasises a unique aspect.

Essay by Rolf Thauer

Joan Broderick and John Peters et al. delve into the biosynthesis of CN and CO ligation in hydrogenases. The biochemical, structural and catalytic properties of the [NiFeSe] hydrogenases are examined by Inês Pereira and Pedro Matias et al., and the structure of the iron guanylylpyridinol cofactor of [Fe] hydrogenase and the implications on the catalytic mechanism of H₂ cleavage are explored by Seigo Shima et al. Much insight into these enzymes has been gained over the years through the use of both structural and functional models – their importance comes through in many of the contributions in this issue. Kazuyuki Tatsu-mi et al. present an overview of thiolate-bridged Fe–Ni models of the active site of [NiFe] hydrogenase, and the chemistry of diiron complexes that contain the chalcogen atoms Se and Te instead of S, which serve as analogues of the [2Fe2S] subunit of [FeFe] hydrogenase, is described by Takahiro Sakamoto, Mohammad El-khateeb and Wolfgang Weigand et al.

As these enzymes are oxygen-sensitive to varying degrees, the need to understand the processes by which O₂ damage occurs is pertinent so as to make them more viable in biotechnological applications. The importance of theoretical and spectroscopic investigations in determining these and other pressing issues are covered too. Marcetta Darensbourg and Wolfgang Weigand address the topic of oxy-

gen-sensitivity in their Microreview. The use of hydrogenases in vivo and as hybrids for H₂ production is reviewed by Erwin Reisner, and the development of functional models of hydrogenases that incorporate inexpensive metals such as cobalt and nickel to serve as electrocatalysts for the oxidation and production of hydrogen is discussed by Morris Bullock et al. Besides these enticing articles, there is much more to be found in this cluster issue; I am sure that you will not be disappointed.

EurJIC has adopted a composite cover for this thematic issue as well; we feel that the essence of the issue is better captured by featuring a number of important contributions on the cover. As we had a difficult task in selecting the papers to be highlighted, we opted to go with an inside cover, the first time for *EurJIC*! Unfortunately still, not all the outstanding contributions could be showcased in this

**Top-notch,
peer-reviewed
papers**

way. We are grateful to the contributors to the cover, Seigo Shima, Erwin Reisner, Claudio Greco and Alexey Silakov, Morris Bullock, Inês Pereira and Pedro

Matias, et al., and to the inside cover, John Peters and Joan Broderick et al., for providing not only top-notch papers, but also excellent artwork.

At this point, I would like to thank our Guest Editors – this issue would not be what it is without them. From the word go, they have been available and enthusiastically involved, giving us invaluable advice and support. No problem was too big a problem! It has been a privilege to work with them. But, of course, the main credit goes to our authors and our reviewers, who worked tirelessly, sometimes, under great pressure, to ensure a stellar issue.

As the chemistry community gets into the full swing of celebrations for the International Year of Chemistry, I hope that you will join us in celebrating this exemplary issue too.

