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Andreas S.J.L. Bachmeier

Metalloenzymes as Inspirational Electrocatalysts for Artificial Photosynthesis

From Mechanism to Model Devices

Doctoral Thesis accepted by
University of Oxford, UK

 Springer

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Supervisor's Foreword

Artificial photosynthesis (AP) research involves designing and building physical systems that mimic natural photosynthesis by using solar energy to convert water into hydrogen and oxygen, leading also to the endothermic conversion of carbon dioxide into organic molecules. If AP could be made efficient and scalable, it would offer a way of storing solar energy as chemical bonds in a 'fuel'. Although it is well known that electricity generated by photovoltaic cells can be used to electrolyse water, it might be advantageous to combine these two steps in a single device. Early research on AP focused on single materials that split water when illuminated, but later research has tried to mimic more closely the modular processes that occur in chloroplasts. Hence, photosynthesis needs a minimum of three components bolted together: (1) the excitation centre (chlorophyll in natural photosynthesis/semiconductor in AP) converts the energy of photons into a separated electron and hole; (2) the fuel-forming electrocatalyst (hydrogenase or ferredoxin NADP⁺ reductase in natural photosynthesis) uses excited electrons to split water and produce hydrogen or organic molecules; (3) the hole-quenching electrocatalyst converts water into oxygen (the oxygen-evolving MnCaO cluster in natural photosynthesis) releases electrons that are required to fill the vacancies ('holes') left in the valence orbitals (or band) when electrons are excited, thus completing a cycle.

In work leading up to 2012, prior to Andreas Bachmeier starting in Oxford as a Graduate Scholar at St John's College, my group had drawn attention to observations we had made regarding the superb efficiency of enzymes as electrocatalysts when attached to suitable electrode materials. Hence, the idea behind attaching enzymes to semiconductors was that the resulting hybrids could provide information on how efficient AP could be, were catalysts as good as enzymes to be available. Enzymes use abundant elements rather than precious metals and they excel at fast, long-range electron transfer with small reorganisation energies. We know the 3D structures of the active sites and have spectroscopic information on different states, and these active sites and surroundings can be systematically modified by genetic engineering.

In his doctoral research, Andreas studied the behaviour of hybrid modular AP systems, investigating several types of enzyme linked to various semiconductors differing in surface properties, bandgap, and energies of valence and conduction bands. His thesis thus combines the principles of structural enzymology with the physical chemistry of semiconductors. Andreas explored different enzyme/material combinations and obtained very interesting results, fostering new mechanistic ideas that resulted in five peer-reviewed publications. One line of reasoning to stem from these experiments was that enzymes are able to 'trap' catalytic electrons, using a combination of distance and low reorganisation energy to compete with destructive recombination (a model also applicable for charge separation in natural photosynthesis).

One of the most pressing problems in AP development is how to scale up economically: at present, researchers are focused on tiny bench-scale demonstrations. Owing to the huge availability of fossil resources, hydrogen and hydrocarbons have little commercial value and it is difficult to encourage any investment by the private sector. Andreas initiated studies of other systems that might give more valuable products than H₂ or C1 compounds. He looked into the possibility of using enzymes containing useful natural chromophores to monitor photo-driven catalytic electron transfer.

In a related project, Andreas worked with Dr. Will Myers to use pulsed EPR spectroscopy to study a particularly active hydrogenase to learn more about its mechanism. Formaldehyde intercepts the catalytic cycle at a highly reduced state, and he was able to propose options for the structure of a highly reduced intermediate of a [FeFe]-hydrogenase trapped by binding of formaldehyde.

Oxford, UK

Prof. Fraser A. Armstrong, FRS

Preface

Artificial photosynthesis, an important route towards future supply of renewable energy, seeks to convert sunlight into storable chemical energy such as fuels. Building upon the principles of biological solar energy conversion, artificial photosynthesis can be broken down into four essential processes: harvesting of visible light, charge (electron–hole) separation, oxidation of water to dioxygen, and fuel formation. Importantly, unlike natural photosynthesis, artificial photosynthesis is solely dedicated to efficient formation of fuels and is not restricted by the availability of arable land.

Both water oxidation and fuel formation require efficient and selective catalysts. This work utilises certain metalloenzymes, which have evolved to catalyse fuel-generating reactions such as the formation of H₂ or the reductive activation of CO₂ to carbon-based fuels with unmatched efficiencies. In contrast to most artificial catalysts, these enzymes are composed solely of abundant elements and operate efficiently at neutral pH. Thus, although not suitable for scale-up, they can be used to mimic conditions under which future devices will have to operate and provide design criteria for the components of applied technologies.

In this thesis, physico-chemical techniques are used to study the mechanism of [FeFe]-hydrogenases, the most proficient H₂-evolving catalysts that rival platinum in activity, by investigating how reversible inhibitors intercept transient enzyme states. The interaction of fuel-forming enzymes with light-absorbing semiconductor electrodes is also explored, leading to the construction of a photoelectrochemical cell for the selective, light-driven reduction of CO₂. Furthermore, this thesis demonstrates that metalloenzymes can be used to establish new directions in artificial photosynthesis research, driving endergonic organic reactions such as specific C=C hydrogenation.

Munich, Germany

Andreas S.J.L. Bachmeier

Parts of this thesis have been published in the following journal articles:

1. How Formaldehyde Inhibits Hydrogen Evolution by [FeFe]-Hydrogenases: Determination by ^{13}C ENDOR of Direct Fe–C Coordination and Order of Electron and Proton Transfers. Andreas Bachmeier, Julian Esselborn, Suzannah V. Hexter, Tobias Krämer, Kathrin Klein, Thomas Happe, John E. McGrady, William K. Myers, and Fraser A. Armstrong, *J. Am. Chem. Soc.* **2015**, *137*, 5381.
2. Enzymes as Exploratory Catalysts in Artificial Photosynthesis. Andreas Bachmeier, Bhavin Siritanaratkul, and Fraser A. Armstrong, in ‘From Molecules to Materials – Pathways to Artificial Photosynthesis’, Eds: E. A. Rozhkova, K. Ariga, Springer **2015**, 99.
3. Solar-driven proton and carbon dioxide reduction to fuels – lessons from metalloenzymes. Andreas Bachmeier and Fraser Armstrong, *Curr. Opin. Chem. Biol.* **2015**, *25*, 141.
4. Selective Visible-Light-Driven CO_2 Reduction on a p-Type Dye-Sensitized NiO Photocathode. Andreas Bachmeier, Samuel Hall, Stephen W. Ragsdale, and Fraser A. Armstrong, *J. Am. Chem. Soc.* **2014**, *136*, 13518.
5. A Multi-Heme Flavoenzyme as a Solar Conversion Catalyst. Andreas Bachmeier, Bonnie J. Murphy, and Fraser A. Armstrong, *J. Am. Chem. Soc.* **2014**, *136*, 12876 (highlighted as ‘JACS-Spotlight’: *J. Am. Chem. Soc.* **2014**, *136*, 13469).
6. How Light-Harvesting Semiconductors Can Alter the Bias of Reversible Electrocatalysts in Favor of H_2 Production and CO_2 Reduction. Andreas Bachmeier, Vincent C. C. Wang, Thomas W. Woolerton, Sophie Bell, Juan C. Fontecilla-Camps, Mehmet Can, Stephen W. Ragsdale, Yatendra S. Chaudhary, and Fraser A. Armstrong, *J. Am. Chem. Soc.* **2013**, *135*, 15026.

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Thanks must also go to my collaborators, without the contributions of whom this work would not have been possible. I am particularly grateful to Dr. William Myers for all his contributions to the work on [FeFe]-hydrogenases and for teaching me (or trying to, at least) a fair bit on pulsed EPR during the many long nights we shared sitting in front of the spectrometer. In this regard, Julian Esselborn is also acknowledged, not only for supplying me with copious amounts of highly concentrated enzyme ('black gold'), but also for his helpful comments regarding mechanistic aspects of [FeFe]-hydrogenases.

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Collaborations

The following collaborators contributed to the work presented in this thesis. Enzyme samples were kindly provided by several laboratories: [FeFe]-hydrogenase enzymes were prepared by Julian Esselborn (laboratory of Prof. Thomas Happe, Ruhr-Universität Bochum, Germany). Carbon monoxide dehydrogenase was provided by Dr. Mehmet Can (laboratory of Prof. Stephen Ragsdale, University of Michigan, USA), and [NiFeSe]-hydrogenase was prepared by Dr. Christine Cavazza, (laboratory of Prof. Juan-Carlos Fontecilla-Camps, Institute de Biologie Structurale, Grenoble). Samples of flavocytochrome c_3 were provided by Profs. Graeme Reid (Institute of Cell and Molecular Biology, University of Edinburgh) and Stephen Chapman (Department of Chemistry, University of Edinburgh).

The pulsed EPR experiments presented in Chap. 3 were carried out together with Dr. William Myers (Centre for Advanced Electron Spin Resonance, University of Oxford), who developed the mathematical framework for data analysis, analysed the data, and prepared the figures. The DFT calculations presented in Chap. 3 were performed by Prof. John McGrady (Inorganic Chemistry Laboratory, University of Oxford).

Some of the electrochemistry experiments presented in Chap. 4 were carried out by Sophie Bell under my supervision, and some of the electrochemistry experiments shown in Chap. 5 were conducted by Samuel Hall, also under my supervision. In both cases, I devised the experiments.

The SEM images presented in Chaps. 4 and 5 were recorded by Prof. Jamie Warner (Department of Materials, University of Oxford).

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Notation

Acronyms and Abbreviations

[2Fe] _H	Two-iron subsite of H-cluster
[Ox]	Concentration of oxidised species
[Red]	Concentration of reduced species
a_i	Activity of component i
a.c.	Alternating current
adt	Azadithiolate
aq	Aqueous
A	Area
	Hyperfine coupling constant
Acetyl-CoA	Acetyl coenzyme A
ACS	Acetyl-CoA synthase
ADP	Adenosine diphosphate
AM 1.5 G	Air mass 1.5 global standard G173
APCE	Absorbed photon-to-current efficiency
Arg	Arginine
Asp	Aspartic acid
ATP	Adenosine triphosphate
B	Magnetic field
bp	Boiling point
bpy	2,2'-bipyridine
Bu	Butyl
C	Capacitance
c	Concentration
Ca	<i>Clostridium acetobutylicum</i>
CaHydA	<i>Clostridium acetobutylicum</i> hydrogenase A
CA	Chronoamperometry
CB	Conduction band
CE	Counter electrode
Ch	<i>Carboxydotherrnus hydrogenoformans</i>

CIGS	Copper indium gallium selenide
Co–Pi	Cobalt phosphate (oxide) oxygen evolution electrocatalyst
CODH	Carbon monoxide dehydrogenase I from <i>Carboxydotherrmus hydrogenoformans</i>
<i>Cp</i>	<i>Clostridium pasteurianum</i>
CPE	Constant phase element
<i>Cr</i>	<i>Chlamydomonas reinhardtii</i>
CrHydA1	<i>Chlamydomonas reinhardtii</i> hydrogenase A1
CV	Cyclic voltammogram
CW	Continuous-wave
Cys	Cysteine
Cyt	Cytochrome
<i>D</i>	Diffusion coefficient
<i>d</i>	Separation distance between two reactants
<i>d</i> ₀	Separation distance in encounter complex
d.c.	Direct current
D1	Photosynthetic protein D1
D2	Photosynthetic protein D2
<i>Dd</i>	<i>Desulfovibrio desulfuricans</i>
DFT	Density functional theory
DSSC	Dye-sensitised solar cell
<i>e</i> [−]	Electron
<i>e</i> ₀	Elementary charge = 1.602×10 ^{−19} C
<i>E. coli</i>	<i>Escherichia coli</i>
<i>E</i>	Electrode potential
<i>E</i> ⁰	Standard electrode potential
<i>E</i> _a	Acceptor level
<i>E</i> _{cb}	Conduction band potential
<i>E</i> _d	Donor level
<i>E</i> _F	Fermi level
<i>E</i> _{fb}	Flat-band potential
<i>E</i> _g	Band gap
<i>E</i> _{oc}	Open-circuit photopotential
<i>E</i> _{on}	Photocurrent onset potential
<i>E</i> _{vb}	Valence band potential
EIS	Electrical impedance spectroscopy
ENDOR	Electron nuclear double resonance
EPR	Electron paramagnetic resonance
EQE	External quantum efficiency
ESEEM	Electron spin echo envelope modulation
EXAFS	Extended X-ray absorption fine structure
<i>f</i>	Force constant
<i>ff</i>	Fill factor
fcc ₃	Flavocytochrome <i>c</i> ₃ from <i>Shewanella frigidimarina</i> NCIMB400
<i>F</i>	Faraday's constant = 96,485 C mol ^{−1}

FAD	Flavin adenine dinucleotide
Fd	Ferredoxin
FDH	Formate dehydrogenase
FID	Free-induction decay
FTIR	Fourier transform infrared spectroscopy
FTO	Fluorine doped tin oxide
G	Gibbs free energy
GC	Gas chromatography
Glu	Glutamic acid
h	Planck's constant = 6.626×10^{-34} J s
\hbar	Reduced Planck's constant = $h/2\pi$
H_2 ase	Hydrogenase
H_{el}	Electronic coupling matrix element
His	Histidine
HOMO	Highest occupied molecular orbital
Hyd1	<i>E. coli</i> hydrogenase I
HYSCORE	Hyperfine sublevel correlation spectroscopy
i	Current
	Imaginary number
i_{ph}	Photocurrent
I	Nuclear spin
	Photon flux
IHP	Inner Helmholtz plane
IPCE	Incident photon-to-current efficiency
IQE	Internal quantum efficiency
IR	Infrared (spectroscopy)
ITO	Indium tin oxide
j	Current density
j_0	Exchange current density
k	Kinetic rate constant
k_B	Boltzmann constant = 1.381×10^{-23} J K ⁻¹
K	Equilibrium constant
KPi	0.1 M potassium phosphate buffer
L	Minority carrier diffusion length
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
Lys	Lysine
M	Metal
m_s	Electron spin quantum number
Me	Methyl
MES	2-(<i>N</i> -morpholino)ethanesulfonic acid
MMCT	Metal-to-metal charge-transfer
MO	Molecular orbital
MPA	3-mercaptopropionic acid

n	Amount of substance
	Electron density, concentration
N_A	Acceptor density
N_D	Donor density
NADP(H)	Nicotinamide adenine dinucleotide phosphate
NHE	Normal hydrogen electrode
NMR	Nuclear magnetic resonance
OEC	Oxygen evolving cluster
OHP	Outer Helmholtz plane
Ox	Oxidised species
p	Hole density, concentration
P_{in}	Incident illumination power density
P1	4-[Bis(4-{5-[2,2-dicyanovinyl]-thiophene-2-yl}phenyl)amino]benzoic acid
P25	TiO ₂ nanopowder: primary particle size 21 nm, 80% anatase/20% rutile
PCET	Proton-coupled electron transfer
PDB	Protein data bank
PEC	Photoelectrochemical cell
PFE	Protein film electrochemistry
PFIRE	Protein film infrared electrochemistry
PGE	Pyrolytic graphite edge
Phe	Pheophytin <i>a</i>
Pr	Propyl
PSI	Photosystem I
PSII	Photosystem II
PV	Photovoltaics
Py	Pyridyl
PZC	Point of zero charge
q	Charge stored on capacitor
Δq	Change in equilibrium bond distance
Q_A	Plastoquinone A
Q_B	Plastoquinone B
Q_BH_2	plastoquinol B
r	Radius
rpm	Revolutions per minute
R	Ideal gas constant = 8.314 J K ⁻¹ mol ⁻¹
	Resistance
RE	Reference electrode
Red	Reduced species
RHE	Reversible hydrogen electrode
RuBisCO	Ribulose-1,5-biphosphate carboxylase-oxygenase
RuBP	Ribulose-1,5-biphosphate
RuP	[Ru ^{II} (bpy) ₂ (4,4'-(PO ₃ H ₂) ₂ bpy)]Br ₂
S	Electron spin

S	State in Kok cycle
SCE	Saturated calomel electrode
SeCys	Selenocysteine
SEM	Scanning electron microscopy
Ser	Serine
SHE	Standard hydrogen electrode
SOMO	Singly occupied molecular orbital
STH	Solar-to-hydrogen
STS	Solar-to-succinate
t	Time
T	Temperature
	Dipolar component of hyperfine interaction
TEOA	Triethanolamine
TOF	Turnover frequency
TON	Turnover number
TST	Transition state theory
UV	Ultraviolet
UV/vis	Ultraviolet–visible absorption spectroscopy
ν	Scan rate
	Kinematic viscosity of the solvent
ν_i	Stoichiometric coefficient of component i
v	Volume
V	Voltage
V_{oc}	Open-circuit voltage
VB	Valence band
wt	Weight
W	Depletion layer width
WE	Working electrode
XAE	X-ray absorption and emission
XAS	X-ray absorption spectroscopy
z	Number of electrons
Z	Impedance
Z_w	Warburg impedance
α	Transfer coefficient
	Absorption coefficient
β	Attenuation factor
ϵ	Dielectric constant
ϵ_0	Permittivity of free space
ϵ_{op}	Optical dielectric constant of the solvent
ϵ_s	Static dielectric constant
ϕ	Electric potential
Φ	Quantum yield
Γ	(electroactive) coverage
η	Overpotential
	Efficiency

$\eta_{e-/h+}$	Absorptance
κ_{el}	Electronic factor
κ_n	Nuclear factor
λ	Wavelength
	Reorganisation energy
μ	Electrochemical potential
$\tilde{\mu}$	Chemical potential
μ_0	Vacuum permeability
μ_B	Bohr magneton
μ_n	Nuclear magnetic moment
ν	Frequency
Θ	Phase difference
ρ	Spin density
τ	Decay constant
	Delay time (EPR)
ω	Rotation rate
	Angular frequency

Units of Measure

‰	Per mille
Å	Ångström
atm	Atmosphere(s)
au	Atomic units
bn	Billion
C	Coulomb(s)
Da	Dalton(s)
eV	Electron volt(s)
F	Farad(s)
G	Gauss
h	Hour(s)
Hz	Hertz
J	Joule(s)
K	Kelvin
L	Litre(s)
m	Metre(s)
M	mol L ⁻¹
min	Minute(s)
Mtoe	Million tons of oil equivalent
ppm	Parts per million
rad s ⁻¹	Radian per second
s	Second(s)
scc	Standard cubic centimetre(s)
S	Siemens
T	Tesla

V	Volt(s)
W	Watt(s)
Ω	Ohm(s)

Prefices

p	Pico (10^{-12})
n	Nano (10^{-9})
μ	micro (10^{-6})
m	Milli (10^{-3})
c	Centi (10^{-2})
k	Kilo (10^3)
M	Mega (10^6)
G	Giga (10^9)
T	Tera (10^{12})
<i>i</i>	iso
<i>meso</i>	Mesoporous
<i>p</i>	Para

Common Subscripts and Superscripts

*	Excited state
‡	Transition state
0	Standard state
a	Anodic
c	Cathodic
cat	Catalytic
ct	Charge-transfer
d	Differential
	Distal
diff.	Diffuse layer
dl	Double layer
e	Electron
eq	Equilibrium
et	Electron transfer
F	Faradaic
	Fermi
H	Helmholtz layer
i	Inner-sphere
in	Incident
iso	Isotropic
lim	Limiting
m	Midpoint
	Metal
o	Outer-sphere

obs	Observed
oc	Open-circuit
ox	Oxidised
p	Pendant
	Product
	Proximal
ph	Photo
r	Reactant
red	Reduced
ref	Reference
s	Solution
sc	Short-circuit
	Space-charge layer
w	Working electrode