Aktuelle Aspekte der Chemie

Vorlesung: „Physikalische Chemie der Solarenergie Konversion“ (Photoelecktrochemie)
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Vorlesungssprache: Englisch
LernWeb Link: https://www.uni-muenster.de/LearnWeb/learnweb2/course/view.php?id=55261
LernWeb Selbsteintragen Passwort: SolarKonversion

Vorlesungsinhalt:

Die Umwandlung von Sonnenlicht in nützlichere Ressourcen wie Elektrizität und chemische Brennstoffe ist eine interdisziplinäre Herausforderung. Konzepte aus den Bereichen der Halbleiterphysik, der Materialsynthese, der Elektrochemie, der Reaktionskinetik sowie der Gerätetechnik kommen zusammen, um innovative Ansätze für die solare Energieumwandlung zu finden. Das Ziel dieser Vorlesung ist es, die Grundlagen der photoelektrochemischen Zellen aus einer physikochemischen Perspektive zu präsentieren, die thermodynamische, kinetische und Transportbetrachtungen sowohl im Bulk als auch an Grenzflächen einschließt. Ein Teil der Vorlesung ist der Beschreibung der Methoden gewidmet, die zur Bestimmung der Leistungsfähigkeit von photoelektrochemischen Zellen verwendet werden. Sobald die Grundlagen geschaffen sind, werden die neuesten Entwicklungen auf diesem Gebiet vorgestellt und diskutiert.

Detailed topics covered in the lecture:

- Introduction
    - The Solar Spectrum
    - What kind of materials can absorb sunlight?
    - Strategies for solar energy conversion: natural photosynthesis, photovoltaics & semiconductor/electrolyte junctions (photoelectrochemical cells)
    - What makes a system a photoelectrochemical cell? (Differences between photovoltaic, photoelectrosynthetic and photocatalytic cells)
    - Examples of photoelectrochemical cells
- Semiconductor Physics
    - Intrinsic vs. extrinsic (doped) semiconductors
    - Types of extrinsic semiconductors: n-type & p-type
    - Effect of doping on semiconductor band structures & Fermi level
    - Bulk semiconductors at non-equilibrium (e.g. under illumination)
        - Possible processes for the photogenerated carriers
        - Effect on band structure: splitting of the Fermi level to quasi-Fermi levels
    - Semiconductor surfaces & Fermi level
    - Semiconductor-Metal contacts (Schottky junctions)
        - With surface states (Fermi level pinning)
        - Without surface states
        - Role of the metal work function on semiconductor band structure (bending)
        - Charge carrier transport across Schottky junctions
            - Majority carriers
            - Minority carriers
        - Ohmic contacts to semiconductors

        - p-n junctions
        - Photocurrents & photovoltage (i-V curve of a Schottky junction)
- Electrochemistry basics
    - Components of an electrochemical cell
    - Cell potentials, formal potentials, half-cell potentials & reference electrodes
    - Measuring interfacial potential differences
        - Definition of the electrochemical potential
        - Determination of cell potential using electrochemical potential (with and without a liquid junction potential drop, i.e. diffusion potential)
    - Ion transport in solution
        - Mobility, ionic conductivity & transference numbers
        - Deriving the mass-transfer equation
        - Mixed migration & diffusion at the electrode: balance sheet analysis
    - Electrode kinetics
        - Derivation of the Butler-Volmer equation
        - Tafel kinetics
        - Marcus-Hush electron transfer theory
        - Gerischer electron transfer model: distribution of energy states at the electrode/electrolyte interface (most applicable for photoelectrochemical systems)
    - The electrochemical double-layer
        - The ideal polarizable electrode
        - Helmholtz compact layer model
        - Gouy-Chapman diffuse layer model
        - Stern's modification
        - Capacitance vs. potential curves
    - Electrode-electrolyte junctions
        - Metals vs. Semiconductors
        - Semiconductor-electrolyte interface: Schottky-junction & band bending
        - I-V characteristic: metal vs. semiconductor (dark)
            - Accumulation, depletion and inversion (for SC-electrolyte interfaces)
        - I-V characteristic: semiconductor (under illumination)
            - Photovoltage and limiting current density
    - Experimental techniques & setups
        - 3-electrode vs. 2-electrode configuration
        - 1- vs. 2-compartment cells
        - The working electrode: how to prepare the photoelectrode
            - Ohmic contact & effect of substrate on "background" electrochemical signals
        - Linear sweep voltammetry
            - I-V response without redox couple: double-layer (dis)charging
            - I-V response with reversible redox couple:
                - Peak current, half-wave potential, Randles-Sevcik plot (scan rate-dependence of the faradaic current)
            - Half-cell photocurrents: 3-electrode configuration
        - Electrochemical impedance spectroscopy
            - How is the impedance of a system measured?
            - Describing the electrode-electrolyte interface
            - Potential-dependent impedance measurements to determine the flat-band potential
            - Definition of the flat-band potential, why is it important?

        - Methods for determination of the flat band potential: Hematite as model system
            - Mott-Schottky analysis (impedance based)
                - Assumptions for Mott-Schottky anaylsis
            - Chopped photocurrent method
            - Gärtner-Butler method
            - Light-saturated open circuit potential
            - Comparison of all methods, which one is more suited?
        - Comparisons between impedance spectroscopy and voltammetry: Hematite as model system
    - Photoelectrochemical water-splitting
        - Why?
        - Efficiencies relevant for photoelectrochemical water-splitting systems
            - Solar-to-Hydrogen efficiency (STH)
            - Applied Bias Photon-to-Current efficiency
            - Incident Photon-to-Current efficiency
            - Absorbed Photon-to-Current efficiency
        - Thermodynamics of water-splitting: oxygen evolution reaction (OER) is most challenging
        - Challenges of semiconductors
            - Stabilization against photocorrosion
            - Challenges with binary oxides
            - Combinatorial approaches to identify new oxides
            - Multinary oxides as alternative: BiVO4 as model system
        - Water-splitting, pH and potentials
            - Pourbaix diagrams
            - Energy barriers in electrocatalysis: the overpotential
            - Different materials with different overpotentials
            - (photo)Electrocatalysts for the OER
            - Effect of electrocatalyst on the semiconductor-electrolyte interface
                - Schottky junctions vs. adaptive SC-electrocatalyst junctions
            - Effect of electrocatalyst surface chemistry on photoelectrochemical performance
            - OER catalysts at intermediate (near neutral) pH
            - Why are membranes necessary in photoelectrochemical cells?
            - Effect of pH gradients (due to buffers) on overpotential of photoelectrochemical cells
                - Mitigation strategies:
                    - ON-OFF cycles
                    - Bipolar membranes
                        - How do bipolar membranes function and how can they be successfully incorporated in PEC cells?
            - PEC reactor designs
                - Wireless monolithic: photocatalytic systems
                - Wired monolithic: The artificial leaf
                    - Triple-junction amorphous Si-Ge PV cell connected to two different electrocatalysts for the HER and OER
                - Monopolar external photovoltaic:

            - Photovoltaic photoelectrochemical cells:
                - *p*-InP/V(III), V(II)/C photoelectrochemical cell
                - Dye-sensitized solar cells: "Grätzel cells"
                    - How to assemble one
                    - Challenges in upscaling
                    - New developments: transition solid-state devices
        - Monopolar with integrated photoabsorber:
            - Water-splitting dye-sensitized solar cells
                - Challenges in chromophore-catalyst assemblies
                - Tuning the chemistry to reach maximum efficiencies
- Final remarks on challenges to photoelectrochemical water-splitting