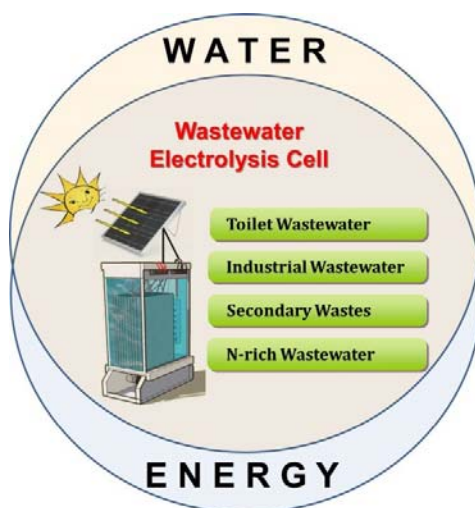


*Chapter 6***OUTLOOK FOR THE FUTURE**

6.1. REACTION NETWORK IN WASTEWATER ELECTROLYSIS CELL

The wastewater electrolysis cell (WEC) for treatment of urea (Chapter 2¹), domestic wastewater (Chapter 3²), and model toilet wastewater (Chapter 4³) showed evidence for the reaction pathway proposed in Figure 6.1. The higher oxide active sites on BiO_x/TiO₂ anode oxidize the Cl⁻ to RCS, which should be transported to bulk phase to oxidize organics to eventually CO₂. The ammonium ions (or other organic N-rich organics such as urea) are oxidized either to N₂ via breakpoint chlorination pathway or to nitrate ions by further oxidation of chloramines. The results in Chapter 2 and 3 demonstrated potential liberation of chlorine radicals (Cl·/Cl₂·) based on *iR*-compensated anodic potential (thermodynamic basis) and enhanced pseudo-first-order rate constants (kinetic basis).^{1,2} Even under the generation of chlorine radicals in bulk phase, the contribution of free chlorine could not be

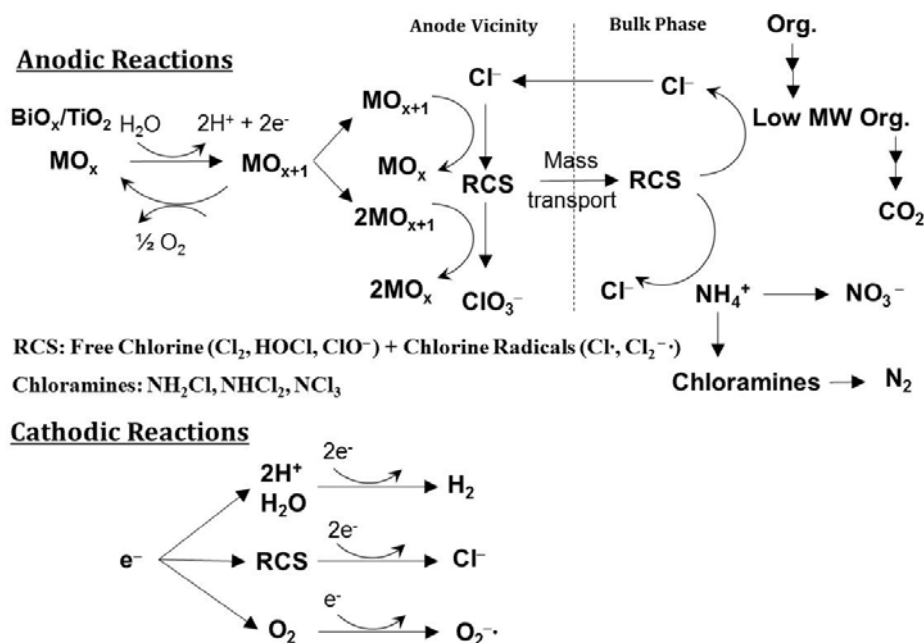


Figure 6.1. Reaction network in wastewater electrolysis cell.

ruled out, due to the facile disproportionation of chlorine radical to free chlorine. The speciation of electrochemically generated RCS was found to be primarily determined by the applied anodic potential and the chloride ion concentration, although a quantitative fractionation was beyond the scope of this study.

On the stainless steel cathodes, water and proton accept electrons to produce molecular hydrogen, while main scavenging reactions include reduction of RCS to chloride ion and molecular oxygen to superoxide radical. In particular, the reduction of RCS results in a null electrochemical cycle reducing the current efficiency both for the desired anodic (pollutants removal) and cathodic (molecular hydrogen generation) reactions.

A presumed facile transition of surface bound hydroxyl radical to higher oxide alleviated the contributions of direct oxidation on the multi-junction $\text{BiO}_x/\text{TiO}_2$ electrodes, prepared as in Table 1.1.¹⁻³ However, the electro-stationary surface concentration of hydroxyl radicals was greatly enhanced in the bilayer hetero-junction anode developed in this study (Chapter 5). Therefore, direct oxidation can be operative on the $\text{Ir}_{0.7}\text{Ta}_{0.3}\text{O}_y/\text{Bi}_x\text{Ti}_{1-x}\text{O}_z$ anodes, as demonstrated by efficient degradations of the formate ion in 50 mM NaCOOH solutions (without chloride ion). With the presence of chloride ion, however, the overall reaction network would be still dominated by mediations of RCS, as in Figure 6.1. Since the molar concentrations of organics in domestic wastewater or human wastes would be much smaller than those of chloride ions, the direct oxidation of organics would be limited by mass transport. Nevertheless, significance enhancements in kinetic constants and current (energy) efficiency are expected when employing the $\text{Ir}_{0.7}\text{Ta}_{0.3}\text{O}_y/\text{Bi}_x\text{Ti}_{1-x}\text{O}_z$ anodes in the wastewater electrolysis cell.

6.2. APPLICATION SCENARIOS OF THE WEC

6.2.1. Toilet Wastewater Treatment. Figure 6.2 shows an application scenario of a photovoltaic (PV) powered WEC system for treatment of wastewater from a public toilet in a developing world, based on the results in Chapter 4.³ A volume balance estimated required the volume of the WEC to be 20 L for handling toilet wastewater from a 30 capita community. An existence of refractory organics in human excreta required a combination with biological pretreatment (septic tank). An energy balance for break-even 24 hours continuous operation predicted the area of the PV panel at 15 m². In more urbanized area, the WEC can also be connected to an existing electric grid, because the power requirement of the WEC operation (0.35 kW) is comparable with running household appliances.

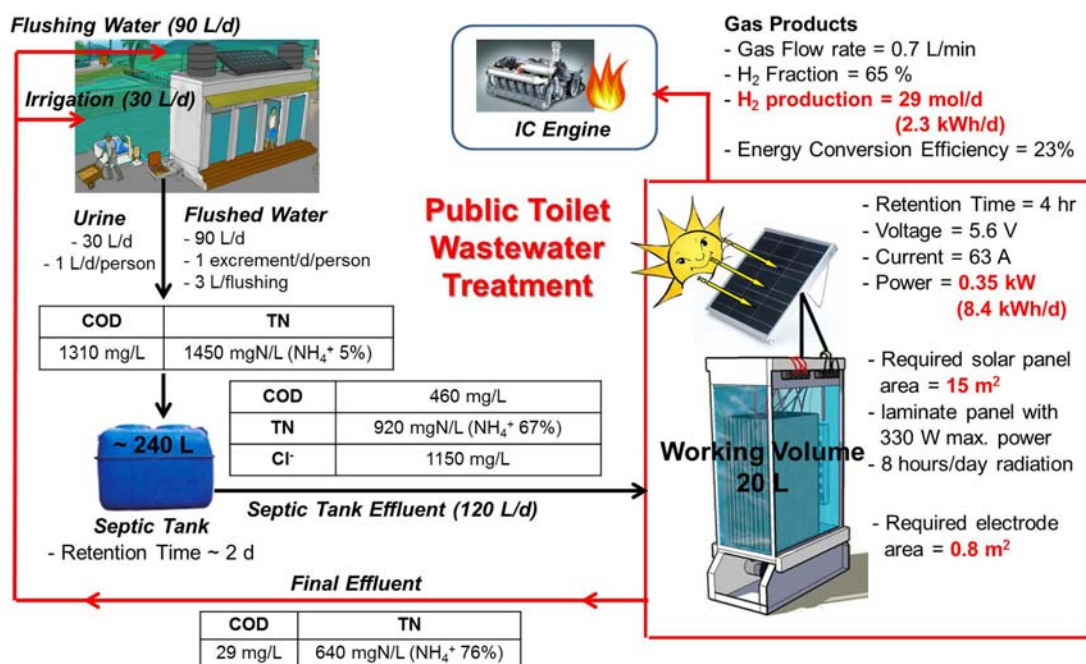


Figure 6.2. Application scenario of wastewater electrolysis cell for treatment of wastewater from a 30 capita public toilet.

US EPA⁴ suggests reclaimed water quality for environmental reuse to satisfy BOD < 30 mg L⁻¹, total suspended solids (TSS) < 30 mg L⁻¹, coliform concentration < 200 CFU 100 mL⁻¹, and residual chlorine > 1 mg L⁻¹. The laboratory and scaled-up experiments (with hydraulic retention time less than 6 h) in Chapter 3 and 4 fully demonstrated the feasibility of effluent reuse for toilet flushing, irrigation, and stream flow recharge.^{2,3} The mixed state molecular hydrogen produced with moderate levels of energy conversion efficiency can be utilized by running a H₂ internal combustion engine.

Consequently, beneficial contributions of the WEC are expected in terms of increased sanitation level, energy saving for wastewater delivery and treatment, alternative water resource by reusing effluents, and fuel production from water-splitting in select cases. When fully assembled a sufficient number of PV panels, a scaled-up PV-powered WEC should be easy to transport to various environments, including urbanized areas, peri-urban environments, and remote locations in the developing world that lack viable sanitation facilities.

6.2.2. Treatment of Other High Salinity Wastewater. The strong oxidation potentials of surface bound hydroxyl radicals and RCS make one envisage that analogous WEC setups can be used for treatment of various kinds of industrial wastewater and secondary waste from environment remediation facilities. Depending on the type of the wastewater, the WEC can be flexibly combined with other physical unit processes to boost the efficacy for remediation and energy storage.

One of the scenarios for industrial wastewater treatment is related with recent progress in Shale gas production. The current method of hydraulic fracturing results in a large

volume of wastewater (flowback water) which carries considerable amounts of suspended/dissolved solids, chloride ion, bromide ion, metals (Ca, Ba, and Sr), and oil/grease.^{5,6} The brine wastewater has been usually treated by a municipal wastewater treatment plant, often causing a deterioration of effluent water quality due to the excessive pollutant loads. The high salinity of the flowback water should let the WEC suitable to an alternative treatment unit process, though the high solids concentration would require a pretreatment for solids/liquid separation. To this end, an electrochemical pretreatment unit with sacrificial anodes (Fe or Al metal) can provide an efficient solids/liquid separation by coagulation and flotation.⁷ In this approach, the dissolving electrodes produce a range of coagulant species. The precipitates from charge neutralization and flocculation can be collected by sedimentation for a given duration or via collision with H₂ bubbles generated on the cathodes surface. Electrolysis is also a well-known technique for generating very fine gas bubbles at sizes smaller than 50 μm. It can be expected that the fine bubbles collide with and attach to the particles and float to the top of the reactor.⁸ Therefore, so-called electroflotation merged with electrocoagulation (electro-coagulation-flotation, ECF) has been investigated for use in treatment of industrial wastewater.⁷

In addition, the WEC makes a perfect fit to treat the brine concentrate from reverse osmosis facilities for desalination or polishing effluents from wastewater or drinking water treatment plants.⁹ The brine water generated in reverse osmosis of wastewater effluent contains biorefractory organics, chloride ion, and nitrate ion (as a byproduct of biological nitrification process). Although a reductive removal of nitrate was not investigated in this study, bimetallic cathodes (*e.g.*, Cu/Zn¹⁰) have been reported to show a strong activity for the reduction of nitrate ion to ammonium ion, which can be degraded to N₂, as thoroughly

discussed in Chapter 2.¹ The effluent from the WEC for treatment of the concentrates can be recycled back to the reverse osmosis unit, if potential chlorinated byproducts from the WEC are of significant concern. Based on the compatibility of the WEC with the reverse osmosis (or other filtration unit process such as nano-filtration), one can further imagine a compact and advanced wastewater treatment processes, which consists of an aerated bioreactor (converting organics to CO_2 and NH_4^+ to NO_3^-), a reverse osmosis for producing purified water, and the WEC to reduce the pollutant loadings of concentrated brine (converting biorefractory organics to CO_2 and NO_3^- to N_2).

The greater selectivity to N_2 in the electrochemical transformation of urea, as shown in Chapter 2,¹ allows for broader application of the WEC for remediation of N-rich wastewater (wastewater from livestock and fish-farm industry, landfill leachate, and anaerobic sludge digester effluents). The WEC is flexible enough to adjust the final products depending on the purposes; *i.e.*, an adjustment of current density or external reactive chlorine generation in a multi-component reactor can increase the yield of nitrate ion for fertilizer production.

6.3. REFERENCES

- (1) Cho, K.; Hoffmann, M. R. Urea degradation by electrochemically generated reactive chlorine species: Products and reaction pathways. *Environmental Science & Technology* **2014**, *In Revision*.
- (2) Cho, K.; Qu, Y.; Kwon, D.; Zhang, H.; Cid, C. A.; Aryanfar, A.; Hoffmann, M. R. Effects of Anodic Potential and Chloride Ion on Overall Reactivity in Electrochemical Reactors Designed for Solar-Powered Wastewater Treatment. *Environmental Science & Technology* **2014**, *48* (4), 2377-2384.
- (3) Cho, K.; Kwon, D.; Hoffmann, M. R. Electrochemical treatment of human waste coupled with molecular hydrogen production. *RSC Advances* **2014**, *4* (9), 4596-4608.
- (4) *Guidelines for water reuse*; EPA/600/R-12/618; United States Environmental Protection Agency: Washington, D.C., 2012.
- (5) Warner, N. R.; Christie, C. A.; Jackson, R. B.; Vengosh, A. Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania. *Environmental Science & Technology* **2013**, *47* (20), 11849-11857.
- (6) Gregory, K. B.; Vidic, R. D.; Dzombak, D. A. Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements* **2011**, *7* (3), 181-186.
- (7) Jiang, J. Q.; Graham, N.; Andre, C.; Kelsall, G. H.; Brandon, N. Laboratory study of electro-coagulation-flotation for water treatment. *Water Research* **2002**, *36* (16), 4064-4078.
- (8) Cho, K.; Chung, C. M.; Kim, Y. J.; Hoffmann, M. R.; Chung, T. H. Electroflotation clarifier to enhance nitrogen removal in a two-stage alternating aeration bioreactor. *Environmental Technology* **2013**, *34* (19), 2769-2776.
- (9) Bagastyo, A. Y.; Batstone, D. J.; Rabaey, K.; Radjenovic, J. Electrochemical oxidation of electro-dialysed reverse osmosis concentrate on Ti/Pt-IrO₂, Ti/SnO₂-Sb and boron-doped diamond electrodes. *Water Research* **2013**, *47* (1), 242-250.
- (10) Li, M.; Feng, C. P.; Zhang, Z. Y.; Shen, Z. L.; Sugiura, N. Electrochemical reduction of nitrate using various anodes and a Cu/Zn cathode. *Electrochemistry Communications* **2009**, *11* (10), 1853-1856.