Hydrogen can be produced directly from solar energy via photoelectrochemical water-splitting redox reactions. To make photo-electrochemical systems more efficient it is desired to be operated at high power and current densities. Using concentrated irradiation increases the operating current density but also heats the cell. Operating the electrolyser system at a higher temperature reduces the required reaction potential to drive the water splitting reaction. The heat from solar cells can be used to increase the electrolyser temperature reducing the overpotential losses and improving the system efficiency.

For this reason several groups have investigated system configuration [1,2] and thermal integration to make photo-electrochemical systems more competitive and cost effective. Beck has developed a framework to understand the effect of system configuration on thermodynamic limiting efficiencies for PV based solar hydrogen generation systems utilizing PV as either as solar cells (PV- Electrolysis) or as photoelectrodes (PEC) or some hybrid in between [3]. Tembhumre et. al. has demonstrated an integrated PEC system operating at higher current densities under concentrated solar irradiation along with thermal integration and mass transport optimization for improving the theoretical maximum efficiency [4]. Though this approach improves the PEC efficiency, it is still not clear that what are the fundamental limits of a solar hydrogen generation system with integrated thermal management and if using such complicated device design is the most optimum way of utilizing the heat.

In this work we present a model to calculate the limiting efficiencies of PV-based solar hydrogen generation systems considering the fundamental losses following the method of Hirst et. al. [5] Solar to hydrogen generation efficiency via water splitting is limited by unavoidable intrinsic losses in the system. Mismatch between the semiconductor bandgap and solar spectrum results in non-absorption of photons with energy lower than bandgap. Photovoltaic efficiency further reduces due to radiative recombination and black body radiation losses. The inequality in the absorption and emission angle of solar radiation results in Boltzmann loss. Photovoltaic system losses maximum energy as thermalization loss due to strong interaction between excited carriers and lattice phonons releasing energy at the bandgap edge. With increase in temperature, photovoltaic efficiency decreases with increase in the thermalization loss. Activation overpotential losses are introduced by the catalyst system increasing the input voltage required for water splitting reaction. But activation overpotential losses and reaction overpotential reduces with increase in temperature, reducing the input voltage required for water splitting reaction.

By thermal integration, we can remove heat from the PV component (suffer losses at higher temperature) to the catalytic component (reduced overpotential losses at higher temperature) utilizing the thermalization energy loss. We demonstrated a detailed analysis of the effect of thermal integration, semiconductor bandgap and electrolyte mass flow rate on the intrinsic losses and the system efficiency. Transfer of heat can be optimized by the mass flow rate of the electrolyte.

In conclusion, we present a systematic study of efficiency of PV-based solar to hydrogen generator systems and their temperature dependence. We further propose thermal integration as a useful technique to improve theoretical maximum efficiency.

References


