The battle for power in decoupled water electrolysis systems

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Nowadays, the many research group interests are focused on decoupled water electrolysis systems. This interest can be understood if one understands the difference between conventional water electrolysis and the decoupled, mentioned here. In conventional water electrolyser, hydrogen and oxygen are produced simultaneously in one space, as a result of which gas separation with membranes and diaphragms is necessary, preventing their mixing and the danger of explosion. In a decoupled electrolyzer, the evolution of oxygen and hydrogen gases are separated spatially or temporary. Spatial here means that hydrogen and oxygen are released in completely separate spaces. In such an electrolyzer design, membranes and diaphragms are not needed. Temporary here means that in a given cell space, oxygen is released in one period of time and then hydrogen is released in another period of time. Again, no need for membranes and diaphragms.

Decoupled gas release is achieved with red-ox mediator auxiliary electrodes. Namely, the cell, as in conventional electrolysis, has two electrodes, where one of the electrodes, the working electrode, serves to realize the hydrogen evolution reaction (HER) or the oxygen evolution reaction (OER), and the other, red-ox mediator auxiliary electrode, replaces the opposite gas evolution reaction with some other reduction or oxidation reaction. For example, the Ni(OH)₂ electrode serves very well as a red-ox mediator in an alkaline environment¹. When HER occurs on the working electrode, Ni(OH)₂ is anodically oxidized to NiOOH, but when OER occurs on the working electrode, NiOOH is reduced back to Ni(OH)₂. It's all a cyclic process that requires only to reverse the polarity of the power supply and ensure that the gases are collected in the right cycle. Another good example is a WO₃ electrode in an acidic environment^{2,3}. When OER occurs on the working electrode, the H⁺ intercalation reaction takes place in the WO₃ electrode at a negative potential, converting the WO₃ electrode to H_xWO₃. When HER occurs on the working electrode, H⁺ is deintercalated from the H_xWO₃ electrode. Both examples demonstrate the successful separation of gases in the electrolysis process. It has even been established that the efficiency of electrolysis is comparable to conventional electrolyzers. Everything seems great, but what about the power?

This work examines the main power-limiting reasons in the decoupled electrolysis process. These reasons are primarily related to the red-ox mediator active substance mass and current-to-mass ratio. The power and energy density of the red-ox mediator material creates this limit. In order to increase the power of the process, it is necessary to create a structure in which the largest possible mass of the active component is loaded. As the mass of the active component in the red-ox mediator electrode continues to increase, a secondary power limit appears due to the conditions of the working electrode. Namely, the potential of the working electrode, which is limited due to the parasitic reactions of the red-ox mediator electrode, is small in order to achieve a higher process current, therefore the process will be limited in power. In this work, the electrolysis process is optimized, where the optimal solution between the two aforementioned limits is found.

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