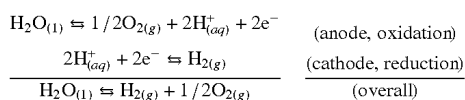


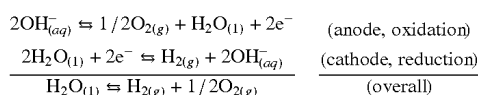
potential, the foregoing reaction (1) may be referred to as a water electrolysis reaction. The water electrolysis reaction may be conducted in an electrochemical cell that includes an anode and a cathode where an oxidation reaction occurs at the anode and a reduction reaction occurs at the cathode. Water electrolysis may be conducted in the presence of an acid or a base.

[0021] In water electrolysis in the presence of an acid, the following reactions occur at the anode and cathode:



[0022] where e^- denotes an electron. At 298 K with all species in their standard states (pure substance for liquids and solids, 1 M for dissolved species, and 1 atm pressure for gases), the half-cell potential of the anode reaction is -1.23 V and the half-cell potential of the cathode reaction is 0 V. (All half-cell potentials reported herein are relative to the normal hydrogen electrode.) The resulting total standard cell voltage E_{Cell}^0 is the sum of the two half-cell potentials and is equal to -1.23 V. The negative total cell voltage indicates that the overall reaction does not occur spontaneously at 298 K and standard state conditions.

[0023] In water electrolysis in the presence of a base, the following reactions occur at the anode and cathode:



[0024] where e^- denotes an electron. At 298 K with all species in their standard states (pure substance for liquids and solids, 1 M for dissolved species, and 1 atm pressure for gases), the half-cell potential of the anode reaction is -0.40 V and the half-cell potential of the cathode reaction is -0.83 V. The resulting total standard cell voltage E_{Cell}^0 is the sum of the two half-cell potentials and is equal to -1.23 V. The negative total cell voltage indicates that the overall reaction does not occur spontaneously at 298 K and standard state conditions.

[0025] In order to effect the water electrolysis reaction in the presence of an acid or a base, a minimum external voltage in an amount equal to the total cell voltage is required. From the above analysis at standard state conditions, 1.23 V is the minimum voltage required to initiate the water electrolysis reaction in the presence of an acid or a base. In practice, it has been found that voltages of about 2.0 V are needed for either reaction to proceed at a reasonable rate. Since the required voltage is high, a significant and costly expenditure of electrical energy is needed to achieve water electrolysis at practical rates.

[0026] The foregoing analysis is predicated on a temperature of 298 K and standard state conditions. Changes in temperature, gas pressure etc. influence the minimum and practical voltages needed to run the water electrolysis reac-

tion. Conditions corresponding to more favorable voltages may be found, but a more rigorous electrochemical analysis shows that reasonable variations in conditions have only a modest effect on the voltages and that conditions considered to be practical may still require high voltages.

[0027] While recognizing that water electrolysis is a feasible approach for producing hydrogen, the instant inventors wish to identify more cost-effective methods. In the co-pending parent U.S. pat. appl. Ser. No. 09/929,940, the disclosure of which has been incorporated by reference hereinabove, the instant inventors considered the production of hydrogen from hydrocarbons and, preferably, oxygenated hydrocarbons. As in hydrogen production from water, the production of hydrogen from most hydrocarbons and many oxygenated hydrocarbons occurs through reactions that are not spontaneous at standard conditions. In these reactions, spontaneity is assessed through the Gibbs energy of reaction, rather than electrochemical cell voltage, where a negative Gibbs energy of reaction corresponds to a spontaneous reaction. Conventionally, hydrogen is produced from hydrocarbons through reformation reactions with water to form hydrogen gas along with carbon dioxide as a by-product. Since these reformation reactions have large and positive Gibbs energies of reaction, high temperatures are required to initiate them and even higher temperatures are required to achieve reasonable hydrogen production rates. The high temperatures provide reaction conditions at which the Gibbs energy of reaction becomes negative. Reformation of oxygenated hydrocarbons (e.g. methanol, ethanol, formic acid, formaldehyde etc.) with water to form hydrogen and carbon dioxide is also possible and frequently occurs through reactions having smaller Gibbs energies of reaction than those of hydrocarbon reformation reactions. In some reformation reactions of oxygenated hydrocarbons with water, small negative values of the Gibbs energy of reaction are observed and these reactions occur spontaneously, albeit slowly, at standard conditions.

[0028] In order to promote the reformation reactions of hydrocarbons and oxygenated hydrocarbons, the instant inventors in the co-pending, parent U.S. pat. appl. Ser. No. 09/929,940 considered factors that may facilitate reformation reactions. The instant inventors recognize the need to identify reactions or conditions that lead to lower, and preferably negative, values of the Gibbs energy of reaction so that hydrogen production is promoted. Preferably, the Gibbs free energy of reaction should be negative at a temperature near or below room temperature in order to achieve efficient room temperature production of hydrogen.

[0029] The co-pending, parent U.S. pat. appl. Ser. No. 09/929,940 by the instant inventors teaches the use of bases as a method for lowering the Gibbs energy of reaction of hydrogen producing reactions that utilize hydrocarbons or oxygenated hydrocarbons as starting materials. Specifically, the instant inventors applied a thermodynamic analysis and demonstrated that reactions of bases with many hydrocarbons or oxygenated hydrocarbons have lower Gibbs energies of reactions and occur at lower temperatures than conventional reformation processes using water and no base. Inclusion of a base leads to hydrogen production along with the bicarbonate ion (HCO_3^-) or carbonate ion (CO_3^{2-}) as by-products. Table 1 shows the extent to which the Gibbs energy of reaction decreases in the presence of a base for reactions that produce hydrogen from methanol.

