equations indicate that ΔG (or ΔG^0) and E_{Cell} (or E_{Cell}^0) have opposite signs. The condition for spontaneity of a reaction may therefore be expressed as a requirement for a negative value of ΔG or a positive value of E_{Cell}.

[0039] The standard cell voltage for the methanol and water electrolysis reactions, along with quantities used in the calculation thereof, are shown in Table 2 below:

TABLE 2

Comparison of the standard cell potential E_{Cell}^0 of the methanol electrolysis and water electrolysis reactions.

Reaction	ΔG^0 (kJ/mol)	n	E^0_{Cell}(V)
$CH_3OH_{(l)} + H_2O_{(l)} \rightleftarrows CO_{2(g)} + 3H_{2(g)}$	8.99	6	−0.016
$H_2O_{(l)} \rightleftarrows H_{2(g)} + \frac{1}{2}O_2(g)$	237.19	2	−1.23

[0040] The data of Table 2 indicate that the standard cell potential of the methanol electrolysis reaction is much less negative than that of the water electrolysis reaction. The negative cell potential of the methanol electrolysis reaction indicates that this reaction does not proceed spontaneously, but the small magnitude of the cell potential indicates that only a small voltage is needed to effect the reaction. The voltage required to initiate a reaction may be defined as the external voltage required to increase the cell potential from a negative value to zero. Based on the data of Table 2, for example, a voltage of 0.016 V is needed to initiate the methanol electrolysis reaction at 298 K and standard state conditions. Voltages above 0.016 V both initiate and accelerate the methanol electrolysis reaction. Much higher voltages are needed to initiate and accelerate the water electrolysis reaction. Accordingly, the methanol electrolysis reaction produces hydrogen under more favorable conditions (e.g. lower operating voltages or lower operating temperatures) than the water electrolysis reaction.

[0041] Although the data of Table 2 are based on a temperature of 298 K and standard state conditions, the general result that the methanol electrolysis reaction lower voltages or lower temperatures to initiate or operate at a given rate. Stated alternatively, the methanol electrolysis reaction requires less external energy to become spontaneous than water electrolysis. The lower required external energy means that methanol electrolysis produces hydrogen with a lower expenditure of energy and that its conditions of operation are more cost effective for a given rate of hydrogen production.

[0042] In other embodiments of the instant invention, hydrogen is produced from an electrochemical reaction of methanol with a base. The base provides a hydroxide ion that is capable of reacting with methanol. In one embodiment, methanol reacts with one equivalent of hydroxide ion according to the following anode, cathode and overall reactions:

$$CH_3OH_{(l)} + 7OH^-_{(aq)} \leftrightarrows HCO^-_{3(aq)} + 5H_2O_{(l)} + 6e^- \quad \text{(anode, oxidation)}$$

$$6H_2O_{(l)} + 6e^- \leftrightarrows 3H_{2(g)} + 6OH^-_{(aq)} \quad \text{(cathode, reduction)}$$

$$CH_3OH_{(l)} + OH^-_{(aq)} + H_2O_{(l)} \leftrightarrows HCO^-_{3(aq)} + 3H_{2(g)} \quad \text{(overall)}$$

[0043] In this reaction, hydrogen gas is produced along with bicarbonate ion as a by-product. Methanol may also react with two equivalents of hydroxide ion to produce hydrogen gas along with carbonate ion as a by-product according to the following anode, cathode and overall reactions:

$$CH_3OH_{(l)} + 8OH^-_{(aq)} \leftrightarrows CO^{2-}_{3\,(aq)} + 6H_2O_{(l)} + 6e^- \quad \text{(anode, oxidation)}$$

$$6H_2O_{(l)} + 6e^- \leftrightarrows 3H_{2(g)} + 6OH^-_{(aq)} \quad \text{(cathode, reduction)}$$

$$CH_3OH_{(l)} + 2OH^-_{(aq)} \leftrightarrows CO^{2-}_{3\,(aq)} + 3H_{2(g)} \quad \text{(overall)}$$

[0044] The amount of base present in the reaction mixture is an important consideration in establishing whether methanol reacts primarily with one or two equivalents of hydroxide ion in the overall reaction. In principle, both reactions can occur simultaneously and in practice, the specific reaction conditions determine whether one overall reaction is more important than the other overall reaction. When small amounts of base are present, overall reaction of methanol with one equivalent of hydroxide is more likely than overall reaction of methanol with two equivalents of hydroxide. As the amount of base increases, however, overall reaction of methanol with two equivalents of hydroxide becomes increasingly more likely and eventually becomes controlling. The concentration of hydroxide ion is an important factor that dictates whether the overall reaction of methanol occurs primarily with one or two equivalents of hydroxide ion. Consequently, the initial pH of the reaction mixture provides an indication of whether methanol reacts primarily with one or two equivalents of hydroxide ion. Thermodynamic data shows that reaction of methanol with one equivalent of hydroxide ion is more likely when the pH of the initial reaction mixture is between about 6.4 and 10.3 and that reaction of methanol with two equivalents of hydroxide ion is controlling when the pH of the initial reaction mixture is above about 10.3. When the pH of the initial reaction mixture is below about 6.4, the reaction of methanol with water is controlling, but reactions of methanol with hydroxide ion may still occur.

[0045] The standard cell potentials of the reactions of methanol with one or two equivalents of hydroxide ion can be calculated using the method described hereinabove. The results of the calculation are shown in Table 3 below: