

TABLE 1

Gibbs Free Energy of Reaction (ΔG_{rxn}) for Hydrogen Producing Reactions of Methanol (25° C., 1 atm. and unit activity of reactants and products)	
Reaction	ΔG_{rxn} (calories)
$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}_2$	4,130
$\text{CH}_3\text{OH} + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{HCO}_3^-$	-4,325
$\text{CH}_3\text{OH} + 2\text{OH}^- \rightleftharpoons 3\text{H}_2 + \text{CO}_3^{2-}$	-9,330

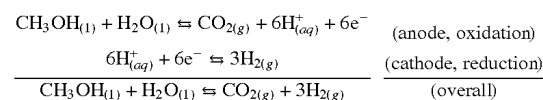
[0030] The first reaction in Table 1 is the conventional reformation reaction of methanol with water. The other two reactions show the production of hydrogen from methanol in the presence of hydroxide ion provided by a base. The table indicates that the conventional reformation reaction is not spontaneous at the stated reaction conditions and that the addition of base leads to spontaneous reactions. The lowering of the Gibbs energy of reaction through the addition of base enables hydrogen production from methanol at room temperature. Alternatively, if temperatures above room temperature are used to enhance the rate of production of hydrogen, the data in the table indicate that inclusion of a base will provide more spontaneous reactions. In the co-pending, parent U.S. pat. appl. Ser. No. 09/929,940, the instant inventors provided exemplary embodiments illustrating the expectations of Table 1 and showed that the production of hydrogen occurs more spontaneously or at a lower practical temperature relative to the conventional reformation reaction when a base is present. Similar results were demonstrated for several other hydrocarbons and oxygenated hydrocarbons.

[0031] In the instant invention, the instant inventors consider methods, other than or in addition to modifying the chemical environment through the addition of a base, which may promote the production of hydrogen. Even though, as described hereinabove, the water electrolysis reaction requires a high electrochemical cell voltage, the principle of using an electrochemical cell voltage to facilitate a chemical reaction is sound and is utilized in the instant invention. An objective of the instant invention is to identify reactions or conditions that produce hydrogen at a lower electrochemical cell potential than is required for the water electrolysis reaction.

[0032] In one embodiment, the instant invention provides electrochemical reactions of organic substances with water that require low electrochemical cell voltages at room temperature. In another embodiment, the instant invention provides electrochemical reactions of organic substances in the presence of an acid or base that require low electrochemical cell voltages at room temperature. In some embodiments, hydrogen production reactions of organic substances occur spontaneously at room temperature in an electrochemical reaction and are accelerated by heating. In other embodiments, hydrogen production reactions of organic substances occur spontaneously at room temperature without applying a voltage and are accelerated by providing a voltage.

[0033] In order to illustrate the principles and scope of the instant invention, the production of hydrogen from methanol in an electrochemical reaction is considered. Although the specific example of methanol is considered in the following discussion, this discussion is not intended to limit to scope of practice of the instant invention. The example of methanol is illustrative of, rather than limiting of, the full scope of the instant invention.

[0034] In one embodiment, hydrogen may be produced from an electrochemical reaction of methanol and water. This embodiment may be referred to as methanol electrolysis and is analogous to the water electrolysis reaction discussed hereinabove. The anode, cathode and overall reactions that occur in methanol electrolysis in the presence of an acid are given below:



[0035] The cell potential of the reaction can be determined from the Gibbs energy change of the reaction using the equation

$$E_{\text{cell}} = -\frac{\Delta G}{nF}$$

[0036] or, at standard conditions,

$$E_{\text{cell}}^0 = -\frac{\Delta G^0}{nF}$$

[0037] where E_{cell} is the cell voltage, ΔG is the Gibbs energy of reaction, n is the number of electrons transferred, F is the Faraday constant

$$\left(F = 96,485 \frac{\text{kJ}}{\text{V} \cdot \text{mol}} \right)$$

[0038] and the superscript 0 indicates standard conditions. The former equation is a general equation that may be used for arbitrary reaction conditions, while the latter equation applies to systems at 298 K and standard state conditions. The latter equation is commonly used because data for ΔG^0 is typically reported in thermodynamic handbooks. Alternatively, ΔG^0 may be computed from Gibbs energy of formation data for the compounds that participate in the reaction and this data is also typically reported at 298 K and standard state conditions. Once the value of the standard cell voltage E_{cell}^0 is known, standard equations can be used to account for deviations of temperature, pressure, concentration etc. from 298 K and standard state conditions. Also, the above

