

TABLE 3

Standard cell potential E_{cell}^0 of reactions of methanol with one or two equivalents of hydroxide ion			
Reaction	ΔG^0 (kJ/mol)	n	E_{cell}^0 (V)
$\text{CH}_3\text{OH}_{(1)} + \text{OH}^-_{(\text{aq})} + \text{H}_2\text{O}_{(1)} \rightleftharpoons \text{HCO}_3^-_{(\text{aq})} + 3\text{H}_{2(\text{g})}$	-26.37	6	0.046
$\text{CH}_3\text{OH}_{(1)} + 2\text{OH}^-_{(\text{aq})} \rightleftharpoons \text{CO}_3^{2-}_{(\text{aq})} + 3\text{H}_{2(\text{g})}$	-47.3	6	0.082

[0046] Table 3 indicates that the reactions of methanol with one or two equivalents of hydroxide ion exhibit positive standard cell voltages. Both reactions therefore occur spontaneously at 298 K and standard conditions without the need to apply an external electrical potential or external heating. The application of an external electrical potential or external heating serves to increase the rate of production of hydrogen relative to standard conditions. The reactions of methanol with hydroxide ion may therefore provide high rates of hydrogen production at low voltages and/or at temperatures at or near room temperature.

[0047] The foregoing discussion of hydrogen production from methanol demonstrates that hydrogen may be produced under more favorable conditions from methanol than from water. The operating voltage or operating temperature required to obtain a given rate of hydrogen production is lower through reactions of methanol compared to reactions of water. Similarly, for a given operating voltage, operating temperature or combination thereof, the rate of hydrogen production from methanol is higher than the rate of hydrogen production from water.

[0048] In addition to methanol, hydrogen may be produced from a variety of organic substances using the instant invention. A preferred characteristic of organic substances suitable for the instant invention is that they be more readily oxidizable than water at a common temperature and corresponding reaction conditions. As used herein, oxidizability refers to the voltage required to initiate a hydrogen producing reaction of an organic substance. In the comparison of methanol electrolysis and water electrolysis discussed in Table 2 hereinabove, for example, initiation of water electrolysis required a voltage of 1.23 V at 298 K and standard conditions and initiation of methanol electrolysis required a voltage of 0.016 V at 298 K and standard conditions. Methanol is thus more oxidizable than water at 298 K and standard conditions. Oxidizability may be similarly defined for temperatures other than 298 K and for non-standard conditions. Pressure, concentration etc. may deviate from standard conditions. Oxidizability further extends to reactions of organic substances with bases where corresponding conditions implies corresponding amounts of base. Organic substances for which conditions can be found such that the organic substance is more oxidizable than water are within the scope of the instant invention. Specific systems include alcohols (methanol, ethanol, etc.), aldehydes (formaldehyde, acetaldehyde, etc.), carboxylic acids (formic acid, acetic acid, etc.), ketones (acetone, etc.), sugars and ethers (dimethyl ether, methyl ethyl ether, diethyl ether, etc.). These

substances may produce hydrogen through reactions with water, water in the presence of an acid, water in the presence of a base and/or a base.

[0049] Bases suitable for use in the instant invention are compounds that provide hydroxide ions. Metal hydroxides are the preferred bases. Representative metal hydroxides include alkali metal hydroxides (e.g. NaOH, KOH etc.) alkaline earth metal hydroxides (e.g. $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, etc.), transition metal hydroxides, post-transition metal hydroxides and rare earth hydroxides. Non-metal hydroxides such as ammonium hydroxide may also be used.

[0050] Methods of producing hydrogen according to the instant invention include combining an organic substance with water and applying a voltage. Other of the instant methods include combining an organic substance with a base and applying a voltage. In a typical experimental configuration, an electrolyte solution containing the organic substance along with water and/or a base is placed in an electrochemical cell that includes an anode and a cathode where a voltage is applied between the anode and cathode to induce or accelerate an electrochemical reaction. A reference or counterelectrode may also be present. The electrodes known in the art are suitable for use in the instant invention. Representative electrodes include those based on carbon, nickel, platinum, transition metals, metal alloys, and hydrogen storage materials. The electrochemical cell may optionally be heated. It is desirable for the voltage applied to be as small as possible so that the energy expenditure is minimized. In a preferred embodiment, the magnitude of the voltage applied is less than 1.0 V. In a more preferred embodiment, the magnitude of the voltage applied is less than 0.5 V. In a most preferred embodiment, the magnitude of the voltage applied is less than 0.25 V.

[0051] In the methods of the instant invention, a conductivity-enhancing agent may also be included in the electrolyte in order to improve conductivity and enhance electrochemical activity. A conductivity-enhancing agent may be useful when the ionizability of the organic substance is low and no other readily ionizable species is present. Ionizability is a measure of a substance's ability to dissociate into ions in solution. Since ions are the preferred charge carriers in an electrolytic solution, it is desirable to have a sufficient number of ions available to insure adequate conductivity to complete an electrochemical reaction. Since most organic substances exhibit low ionizability, electrochemical reactions of organic substances typically require the presence of an ionizable compound in the electrolyte solution. The conductivity-enhancing agent may or may not participate in

