Potassium hydride Hypothesis

The "abnormal"proprieties of the gas mixture resulted from a common duct alkaline electrolytic cell are attributed to an exotic species called Brown Gas, HHO, Hydroxy or EEW (Electrically Expanded Water).

Science rejects that species and name the stoichiometric mixture simple oxy-hydrogen.
http://en.wikipedia.org/wiki/Oxyhydrogen

Still, the oxy-hydrogen mixture could not produce the same effects in – as example – enhance of hydrocarbon fuels or – sometimes – in welding, melting or fusing materials with the electrolytic gases like some electrolytic gases in some conditions.

I present a hypothesis that may explain the proprieties of electrolytic gases.

Potassium Hydride or Sodium Hydride
(depend on the cation used as electrolyte).

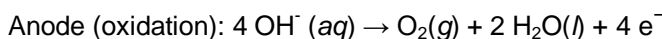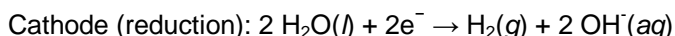Water electrolysis is described below:

"In pure water at the negatively charged cathode, a reduction reaction takes place, with electrons (e^-) from the cathode being given to hydrogen cations to form hydrogen gas (the half reaction balanced with acid):

> Reduction at cathode: $2 H^+(aq) + 2e^- \rightarrow H_2(g)$
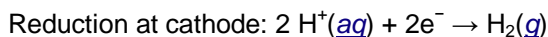
At the positively charged anode, an oxidation reaction occurs, generating oxygen gas and giving electrons to the anode to complete the circuit:

> Anode (oxidation): $2 H_2O(l) \rightarrow O_2(g) + 4 H^+(aq) + 4e^-$
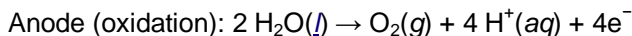
The same half reactions can also be balanced with base as listed below. Not all half reactions must be balanced with acid or base. Many do, like the oxidation or reduction of water listed here. To add half reactions they must both be balanced with either acid or base.
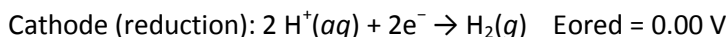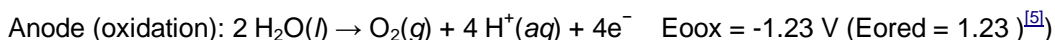
> Cathode (reduction): $2 H_2O(l) + 2e^- \rightarrow H_2(g) + 2 OH^-(aq)$

> Anode (oxidation): $4 OH^- (aq) \rightarrow O_2(g) + 2 H_2O(l) + 4 e^-$

Combining either half reaction pair yields the same overall decomposition of water into oxygen and hydrogen:

> Overall reaction: $2 H_2O(l) \rightarrow 2 H_2(g) + O_2(g)$
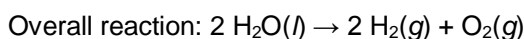
The number of hydrogen molecules produced is thus twice the number of oxygen molecules. Assuming equal temperature and pressure for both gases, the produced hydrogen gas has therefore twice the volume of the produced oxygen gas. The number of electrons pushed through the water is twice the number of generated hydrogen molecules and four times the number of generated oxygen molecules.

Thermodynamics of the process

Decomposition of pure water into hydrogen and oxygen at standard temperature and pressure is not favorable in thermodynamic terms.

> Anode (oxidation): $2 H_2O(l) \rightarrow O_2(g) + 4 H^+(aq) + 4e^-$ Eoox = -1.23 V (Eored = 1.23)[5])

> Cathode (reduction): $2 H^+(aq) + 2e^- \rightarrow H_2(g)$ Eored = 0.00 V

Thus, the standard potential of the water electrolysis cell is -1.23 V at 25 °C at pH 0 (H^+ = 1.0 M). At 25 °C with pH 7 (H^+ = 1.0×10^{-7} M), the potential is unchanged based on the Nernst equation.

However, electrolysis will not generally proceed at these voltages, as the electrical input must provide the full amount of enthalpy of the H_2-O_2 products (286 kJ per mol).

This takes the theoretical and real observed threshold of electrolysis to (-)1.48 V. This is a standard value derived from basic energy conservation for H_2 with a known molar enthalpy value of 286 kJ, (diatomic H_2 having 2 Faraday units of charge per mol), therefore the ideal voltage becomes 286,000/(2*96485) = 1.48 V.

The negative voltage indicates the Gibbs free energy for electrolysis of water is greater than zero for these reactions. This can be found using the $G = -nFE$ equation from chemical kinetics, where n is the moles of electrons and F is the Faraday constant. The reaction cannot occur without adding necessary energy, usually supplied by an external electrical power source.

If the above described processes occur in pure water, H^+ cations will accumulate at the anode and OH^- anions will accumulate at the cathode. This can be verified by adding a pH indicator to the water: the water near the anode is acidic while the water near the cathode is basic. The negative hydroxyl ions that approach the anode mostly combine with the positive hydronium ions (H_3O^+) to form water. *The positive hydronium ions that approach the negative cathode mostly combine with negative hydroxyl ions to form water. Relatively few hydronium (hydroxyl) ions reach the cathode (anode). This can cause a concentration overpotential at both electrodes.*

Pure water is a fairly good insulator since it has a low autoionization, $K_w = 1.0 \times 10^{-14}$ at room temperature and thus pure water conducts current poorly, $0.055 \ \mu S \cdot cm^{-1}$.

Unless a very large potential is applied to cause an increase in the autoionization of water the electrolysis of pure water proceeds very slowly limited by the overall conductivity.

If a water-soluble electrolyte is added, the conductivity of the water rises considerably. The electrolyte disassociates into cations and anions; the anions rush towards the anode and neutralize the buildup of positively charged H^+ there; similarly, the cations rush towards the cathode and neutralize the buildup of negatively charged OH^- there. This allows the continued flow of electricity.

The following cations have lower electrode potential than H^+ and are therefore suitable for use as electrolyte cations: Li^+, Rb^+, K^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, and Mg^{2+}. Sodium and lithium are frequently used, as they form inexpensive, soluble salts.

"...... strong bases such as potassium hydroxide (KOH), and sodium hydroxide (NaOH) are frequently used as electrolytes due to their strong conducting abilities."

http://en.wikipedia.org/wiki/Electrolysis_of_water

$$2H_2O \longrightarrow 2H_2 + O_2$$
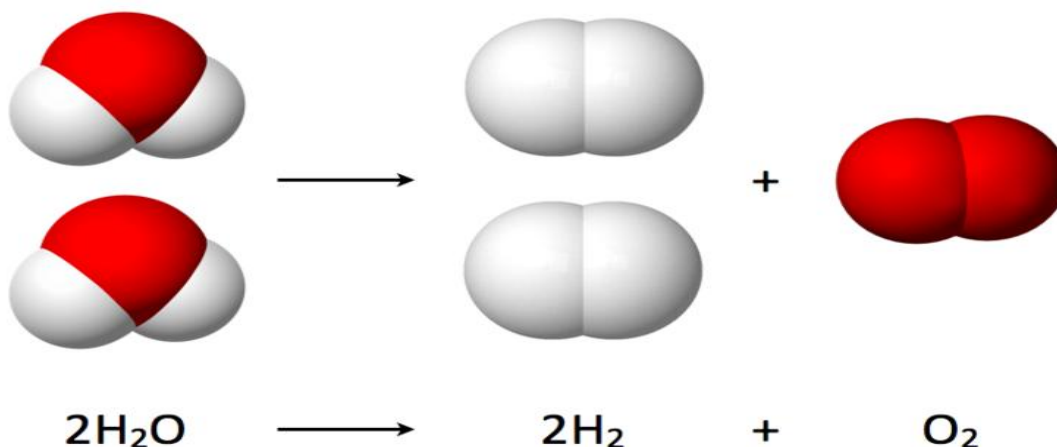
Considering the alkaline electrolyte most usual in electrolytic generation of Hydrogen and Oxygen in industrial grade PEM generators then indeed only separated H2 and O2 can be obtained with electrolyte temperature in range of 90^0 C, 30% KOH concentration and 1.8 Volts.

Considering the alkaline electrolyte for semi-industrial common duct electrolytic cell with the voltage equal or higher than 2 Volts, then lower KOH concentration can be used and the gas mixture Oxyhydrogen – H2 and O2 more or less in perfect stoichiometric ratio - can be obtained.

At that voltage per cell the current drawn is higher and a strong reaction occurs.
Due electrochemical collateral events the cell will be heated to thermal runaway - so cooling procedures are applied.

But, in a common duct electrolytic cell IF the voltage is lower than 2 V the temperature is lower and can be maintained below 60 C^o.
Now, considering that Potassium melting point is 63.5 C (http://en.wikipedia.org/wiki/Potassium)
it can be presumed that once the cell temperature is maintained under a value < 60C^o it is possible that H (monatomic Hydrogen – Protium) evolved from cathode to not combine in diatomic H2.
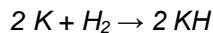It may bond with K^+ solvated ion.

KH
(Potassium Hydride)
http://en.wikipedia.org/wiki/Potassium_hydride

may be formed.
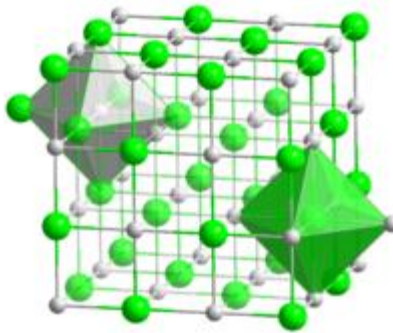
"Potassium hydride is produced by direct combination of the metal and hydrogen:

$2\ K + H_2 \rightarrow 2\ KH$

This reaction was discovered by Humphry Davy soon after his 1807 discovery of potassium, when he

noted that the metal would vaporize in a current of hydrogen when heated just below its boiling point.

Potassium hydride is soluble in fused hydroxides and salt mixtures, but not in organic solvents."

Considering the alkaline environment (the electrolyte) then KH $^-$ could "survive" as gas and can be transferred, collected and stored.
Slight vacuumed cell is a probably a favorable condition.

Inside the piston chamber of ICE the KH reaction with H2O (from intake air humidity or from previous un-exhausted combustion gases) lead to further reactions releasing the monatomic Hydrogen and KOH

2 KH+2H2O=2KOH+4 H
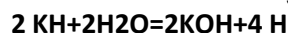
Protium will react with Oxygen to form water

4H+O2=2H2O
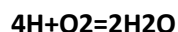
KOH may react with NOx from previous power stroke non-exhausted gases to produce an oxidizer and one more monatomic Protium.

KOH + NOx=KNOx + H

Now, combustion of hydrocarbon in presence of KNOx as oxidizer is enhanced.
Oxidation of monatomic Hydrogen (now 5 atoms from every 2 KH molecules obtained by this special electrolysis) release more thermal energy than H2 from normal electrolysis.

Overall, in certain conditions the electrolysis process can improve the combustion of hydrocarbon and in same time release more water in the piston chamber.
That water contribute thermodynamic efficiency of ICE (improving the heat to pressure conversion) and is also a NOx controlling method.

Nevertheless the yield of gas production from this special electrolysis - low voltage will be reduced the current - but common duct series cells may balance the gas volume reducing the battery voltage to desired value 1.6-1.7 volts and controlling the temperature in same time.

Indeed the H2 and O2 will be also produced by electrolytic process as well and the total mixture become dangerous if compressed since KH and O2 may react due pyrophoric proprieties of KH.

Above described hypothesis correspond with description of conditions, electrolytic cell design and parameters from most of successful implementation of fuel saving devices based on named HHO, Hydroxy, EEW.

$$\Delta H^0 (4H+O2) = 449 \underbrace{\quad}_{O=O} - 5(\underbrace{463)}_{O-H}$$

$$\Delta H^0 (4H+O2) = 449- 2315$$

$$\Delta H^0 (4H+O2) = - 1866 \text{ kJ}$$

Instead of

$$\Delta H° = [2(436) + 499] - 4(463)$$
$$\underbrace{}_{H-H}\underbrace{}_{O=O}\underbrace{}_{O-H}$$

$$\Delta H° = 1371 - 1852$$

$$\boxed{\Delta H° = -481 \text{ kJ}}$$

http://www.chem.tamu.edu/class/majors/tutorialnotefiles/enthalpy.htm