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HYDROGEN-BASED UTILITY ENERGY STORAGE SYSTEM

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Abstract

SRT Group, Inc. (SRT), a leader in innovative energy processes involving halogens, has developed and patented an innovative electrical energy storage and hydrogen production system. The SRT system stores off-peak electricity and produces hydrogen via a novel natural gas/steam thermo-electrochemical process. The following economic analysis indicates that the system can provide on-peak electrical power competitive with natural gas-fueled peaking-turbines and can co-produce hydrogen at costs considerably below that of delivered merchant hydrogen. Preliminary market estimates indicate a $250 million U.S. and $400 million world annual market potential for the SRT system. Competitiveness is achieved due to: (1) the cost for the SRT system is allocated between two products and revenue sources, namely hydrogen and electric energy storage; (2) a very high 89% utilization factor; (3) reducing high-cost electrical needs with low-cost natural gas; and (4) low capital investment. Based on the promise of SRT's early investigations and analysis, the U.S. Department of Energy (DOE) agreed to cost-share 50% of the cost to develop the processes under the auspices of an SRT/DOE Cooperative Agreement. The SRT/DOE program has been in place since 1995 and is culminating with a planned integrated system demonstration in Palm Desert, California and Laramie, Wyoming. The proposed demonstrations will convert intermittent wind energy to provide uninterruptable and reliable electrical energy to the electric grid and produce merchant hydrogen.

Introduction

SRT is a small technology-oriented firm with a business focus on developing and licensing renewable energy technologies. It supports its R&D activities through internal resources, as well as grants and contracts from the federal government. Currently, SRT is developing an electrical energy storage and hydrogen production concept through cost-shared programs with the DOE. This concept requires the integration of two sub-systems or components.

The first is a hydrogen/bromine regenerative electrochemical cell that is well-suited for energy storage applications such as peak shaving, load management and other emerging distributed utility applications. A regenerative hydrogen/bromine cell facilitates electrical energy storage by consuming electricity in electrolyzing hydrogen bromide into hydrogen and bromine reactants as stored chemical energy. The hydrogen and bromine are later reacted electrochemically in the cell to produce electrical energy. Hence, the cell is regenerative (reversible), in that it can efficiently operate as an electrolysis cell producing reactants and consuming electricity or as a fuel cell consuming reactants and producing electricity. In effect, the cell operates as a battery, exchanging electrical and chemical energy, with one difference: the reactants are stored outside of the cell as opposed to a battery where the reactants are inside. Therefore, to increase capacity (kWh) it is only necessary to add more reactants rather than more batteries.

This electrochemical cell technology was originally developed in 1979 by General Electric Co. and was later demonstrated by United Technologies Corporation under DOE and DOD programs. DOE interest in the technology was in response to the 1970's Arab embargo for providing energy storage to reduce the nation's dependence on oil-fueled power generation. The DOD's interest in the 1980's was to provide an electrochemical break, or division between the electric grid and missile silos to prevent EMF damage. Innogy Technologies has developed an industrial-scale, bromine-based regenerative cell for electric utility energy storage. The Innogy cell has been designed for high-volume, low-cost manufacturing and will be adapted for service in the SRT system.

The second component is a chemical reactor that thermochemically produces hydrogen bromide (HBr) and carbon dioxide (CO_2) from water (H_2O), natural gas (CH_4) and bromine (Br_2). The regenerative cell and chemical reactor integrated in a system produces hydrogen and stores electrical energy.

Discussion

In the SRT system, the hydrogen/bromine regenerative cell is used both as a fuel cell to generate electricity and as an electrolyzer to produce marketable hydrogen. Due to its reversible operation, it is used in an energy storage system, storing and dispatching electricity during off-peak and on-peak periods. Off-peak periods are those times of the day (typically at night) when the utility has excess generating capacity and electricity energy is inexpensive due to oversupply. On-peak energy is the opposite; the generating capacity is fully used and electricity is expensive. Thus, utilities have a 'time-of-day-rate' for industrial customers, which reflects the cost difference between on-peak and off-peak energy. Generally off-peak periods are much longer than on-peak periods. This difference between length of periods provides an opportunity to produce more hydrogen than what is required for its fuel cell (on-peak discharging) mode providing excess or supplemental hydrogen bromide electrolyte is available during the electrolysis (off-peak charging) mode.

The technology under development by SRT is a thermo-electrochemical process whereby hydrogen bromide electrolyte is produced from natural gas, water and bromine. The integration of this chemical reactor with the regenerative cell provides a dual-functional system designed to serve both as an electricity load-leveling device and as a hydrogen producer. The block diagram below illustrates the integrated dual-function system.

SRT ENERGY STORAGE / HYDROGEN PRODUCTION SYSTEM

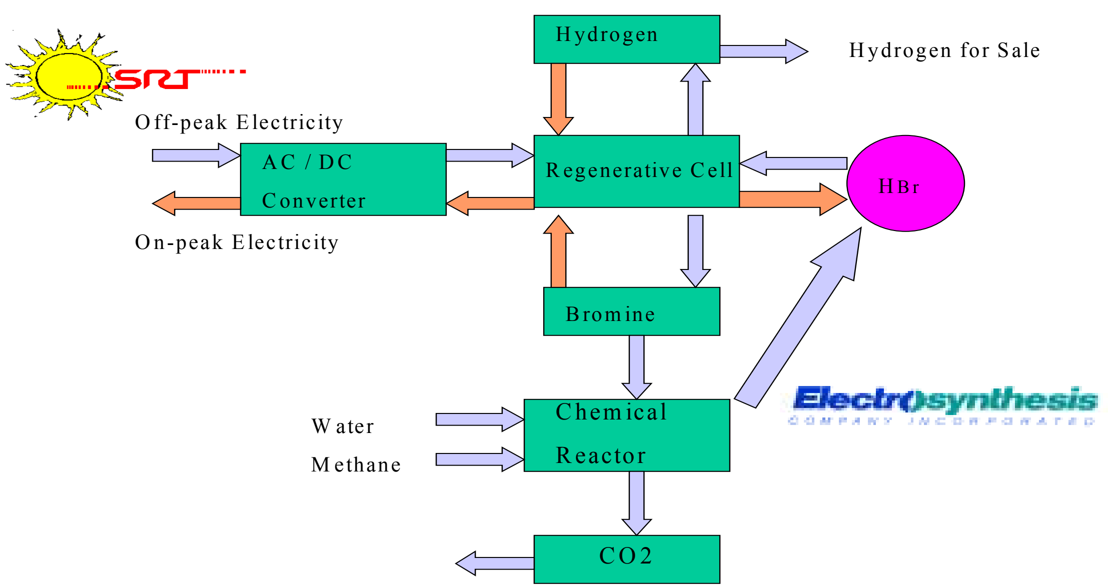

Figure 1: Block Flow Diagram of the SRT Energy Storage/Hydrogen Production System

Technical Background

Electrolysis is currently the most practical method for producing small and moderate quantities of hydrogen (< 1 million scfd). Electrolysis also produces the purest hydrogen. However, hydrogen produced from water electrolysis is relatively expensive. This is due to the high capital cost of the electrolysis cells and electrical energy requirements. Electricity is an expensive, high-value source of energy when compared to other sources such as coal, natural gas or gasoline. Hence, a process that reduces the amount of electrical power required to produce a given amount of hydrogen is very advantageous. How a reduction in electrical energy costs translates into a reduction in hydrogen production costs becomes apparent by comparing the differences in theoretical or ideal cell voltages needed to electrolyze HBr vs. H_2O.

The theoretical cell voltage of HBr is 0.555 Volts and that of H_2O is 1.229 Volts. Actual voltage for commercial electrolysis (which includes inefficiencies and parasitic losses) generally range from 0.9 - 1.0 Volts and 1.8-2.2 Volts for HBr and H_2O, respectively. One Volt is the equivalent of 12.06 kWh/lb of hydrogen. Thus, the electrolysis of HBr requires from 9.65 - 10.85 kWh/lb of hydrogen produced. Water, in comparison, requires 21.71-26.53 kWh/lb. Accordingly, electrolyzing HBr instead of water can reduce electrical energy requirements by over 50 percent. Work by Rockwell International has demonstrated HBr electrolysis at about 0.6 Volts; this is less than one-third the voltage required for water electrolysis using current technology.

Thus, by forming HBr as an intermediate hydrogen carrier from water and bromine, the energy cost, which is the largest cost element of electrolytic hydrogen, is significantly reduced. As an example, if electricity costs $.02/kWh and natural gas costs $2/MBtu, the SRT process substitutes roughly $6.00 of high-value electrical energy with $2.00 worth of lower-value natural gas. Electrical power requirements are a major expense factor that conspires against widespread electrolytic hydrogen production.

Additionally, when recombining hydrogen and bromine in a fuel cell, up to 90% of the chemical energy stored in the reactants can be recaptured as electricity, versus only about 50% for state-of-the-art hydrogen/air fuel cells. This leads to an electric-to-electric efficiency approaching 80% for the system versus 40% for hydrogen/air and 35% for most fossil fuel-fired power generators. In fact, the electrical characteristics of the hydrogen/bromine fuel cell can be compared to a battery in terms of response time, with the major difference that it is only necessary to increase the amount of chemical reactant to increase capacity (kWh). Other benefits afforded by hydrogen bromine are reduced capital and O&M costs.

Technical Concept

Under the auspices of the DOE Hydrogen Program, SRT has over the last five years investigated extensively the photochemical reaction between bromine, steam and solar energy at elevated temperatures for the production of HBr:

$$H_2O + Br_2 + \text{solar energy} \rightarrow 2\ HBr + \tfrac{1}{2}O_2 \qquad \Delta H^o_{298} = +138.34\ \text{kJ/mol} \qquad (1)$$

The HBr is subsequently electrolyzed into H_2 and Br_2, in a regenerative cell:

$$2\ HBr + \text{Electricity} \leftrightarrow H_2 + Br_2 \qquad (2)$$

The hydrogen is stored for sale or power generation, while bromine is either stored or returned to the reactor for further HBr production.

Solar energy is not always available (at night, during cloudy weather or at high latitudes) and where it is available, the hardware to collect it is expensive. SRT found that the capital costs and intermittent nature of solar energy made the process uneconomical with today's economic conditions of low-cost fossil fuels. In an effort to reduce the capital cost and siting limitations inherent in using solar energy, SRT investigated an alternative reaction for producing HBr. This reaction adds methane to equation 1:

$$2\,H_2O + 4\,Br_2 + CH_4 \rightarrow 8\,HBr + CO_2 \qquad \Delta H^o_{298} = -256.99 \text{ kJ/mol} \qquad (3)$$

Thus the chemical energy available from methane can substitute for solar energy. This also has the effect of simplifying the process and making it economically attractive. Thermodynamic calculations performed by researchers at Sandia National Laboratory, California confirmed that this would be a useful avenue of investigation. SRT personnel built and tested a laboratory-sized bromine/steam/methane reactor. Preliminary results showed that HBr could be produced from bromine, steam and methane at a conversion rate of 95% at 750°C without a catalyst.

An alternate reaction to produce HBr without co-producing the greenhouse gas CO_2, is to react bromine with methane to produce HBr and solid carbon. The carbon can be sequestered as a marketable product. This reaction as shown in equation 4, is also being investigated in the SRT/DOE Sandia program.

$$2\,Br_2 + CH_4 \rightarrow 4\,HBr + C \qquad \Delta H^o_{298} = -140.16 \text{ kJ/mol} \qquad (4)$$

Based on these investigations, SRT has integrated its new hydrogen production processes utilizing the bromine-methane reactions with regenerative HBr cells incorporated in its energy storage approach.

Hydrogen/Bromine Energy Storage

The possibility of using a reversible hydrogen/halogen cell for electric energy storage was first suggested in 1964. The proposed system includes a solid polymer electrolyte (SPE) cell, power conditioner and storage for hydrogen, bromine and hydrogen bromide.

The hydrogen/bromine energy storage system has definite advantages over other battery systems:

(1) the hydrogen and bromine electrodes are fully reversible allowing very high electric-to-electric efficiencies;
(2) the same electrodes can be used as electrocatalysts for both chemical and electricity generation and therefore, the same cell can be used for both functions;
(3) the cell is capable of operating at a high current and high power density in both modes, resulting in lower capital costs;
(4) reactants for chemical and electricity generation are stored separately from the cell which makes it cost effective for both peaking and load leveling (weekly cycle) and low-cost capacity (kWh) increases;
(5) also, the components are low cost (plastics and composites).

The major disadvantage of the hydrogen/bromine energy storage system is its use of bromine. Bromine, the only liquid non-metal element known, is a dark red, fuming liquid. It is reactive and corrosive and has a substantial vapor pressure at room temperatures. However, bromination is an essential chemical process with related industrial safety, material and operating standards well known. Because of bromine's toxicity the proposed system draws on the vast experience available from the related chlor-alkali industry.

Design safety features of the hydrogen/bromine energy storage system include:

1) selection of highly reliable equipment, only tried and tested equipment;
2) high safety factor, 50% (rather the usual 10%), minimal use of valves and flanges;
3) all purges and vents discharge through neutralizing and disposal systems;
4) complete modularization of the system with computer monitoring of all operations;
5) enclosure with a slight negative pressure, with air discharge through a neutralizing wash;
6) incorporation of monitors to detect incipient failure and interlocking systems to stand-down a faulty module while the remainder of the plant operates;

and finally, in the event of an undetected chemical leak, passive neutralization systems are employed. This is achieved by using crushed limestone beds to neutralize bromine and hydrobromic acid into benign salts.

Users of the SRT system will have to fully identify its economic strengths and siting limitations before determining its market niche. A review of the earlier (1970-79) development work concluded that there are three primary siting opportunities: 1) industrial; 2) utility; and 3) remote sites. The requirements for each application are indicated in Table 1 below.

Table 1 Comparison of Siting Requirements for the HBr Energy Storage System

Environment	Safety	Utilities available to site	On-site required utilities
Industrial site, factories all around & proximity of other workers at other plants	Highest degree of safety required with every type of safety device available; independently contained modular systems.	Treated water, electric power, fuel oil and natural gas.	Soften water, fire-fighting water, effluent storage and treatment, electric power network.
Utility site, proximity of workers at other plants.	Same as industrial site.	Cooling water, soften water, steam, compressed air, electric power, fuel oil, and natural gas.	Same as industrial site.
Remote site, deserted area, no facilities or workers nearby.	Low degree of safety required, equipment might be in open air.	Raw water, electric power.	Same as industrial site.

Conclusions

1. The hydrogen produced by the SRT system can be used as a chemical feedstock or as an energy carrier.
2. The concurrent R&D program has been successful on the 10 kw program.

3. Phase 1 of the demonstration project is fully funded.

4. The partnership of Department of Energy, SRT Group, State of Wyoming, Wyoming Business Council, Western Research Institute, Innogy Technologies, Electrosynthesis Corporation, SunLine Transit Agency, and SunLine Services Group is a major cooperative with multi-state implications.

5. The 50 kw unit is in evaluation.

6. The testing facility is completed and test drawings are in progress.

Future Work

1. Completion of test stand plans and specifications.

2. Test Stand fabrication.

3. Procurement of test equipment.

4. Installation and checkout of the 50 kW unit.

5. Test and Evaluation of the 50 kW Unit.

6. Preparation of commercialization plan.

References

Analysis of the Merchant Electrical Energy Storage/Hydrogen Production system under Development by SRT Group, Inc. January 2000. A report prepared for the U.S. Department of Energy by the SRT Group, Inc.