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Low-temperature H_2O_2-powered actuators for biorobotics: thermodynamic and kinetic analysis

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***Abstract*—The need for novel, high performance actuators felt in several fields of robotics, such as assistive or rehabilitative robotics, is not fully satisfied by current actuation means. This fosters an intense research on novel energy transduction methods. In particular, propellant-based chemical actuators, able to directly convert chemical energy into mechanical energy, appear very promising, although their potential in robotics has not yet been deeply investigated. This work focuses on H_2O_2, used as propellant for actuators. This chemical was first used in robotics, with excellent results, by Goldfarb and collaborators, in 2003. H_2O_2 dissociation is strongly exothermic, which generates important design issues when the actuated machine operates in close proximity to the human body. In this paper it is shown that: 1) is possible to operate the decomposition process at acceptable temperature, by means of basic solutions of hydrogen peroxide; 2) for basic pH solutions, tin becomes an effective catalyst for H_2O_2 dissociation. A kinetic model of H_2O_2 dissociation in basic solutions is provided, that is in good agreement with experimental data. We show how the model can be used to gather the necessary information for the dimensioning of H_2O_2-based actuators.**

I. Introduction

Hydraulics and pneumatics (water, wind, steam) have been the only means of actuation for centuries. Even the first industrial robot ("Unimate" by Unimation, 1961) was hydraulically operated. The first fully electrical robot was built in the following decade ("PUMA" by Unimation, 1978), and it can be stated that not much has changed in the actuation principles since then. At present, electric (linear and rotary) motors are the elective solution for a large number of applications. Pneumatic and hydraulic actuators also have an important role, thanks to their high power density. Actually, electromagnetic, hydraulic, and pneumatic actuators all have energy densities larger than that of human muscles (about $50\,\mathrm{W}\cdot\mathrm{kg}^{-1}$), while many others (including piezoelectric, magnetostrictive, IPMC) are far below it. Other actuators, such as NiTi alloys based actuators, have very high power density, but specific drawbacks (for NiTi: short life cycle, slow response, and difficult controllability). The current paradigm for robot design also originated around the above-mentioned actuators. The paradigm consists of a consolidated body of knowledge regarding actuator choice criteria, how the machine structure can be built around them, and how the whole system can be controlled. But, as machines get closer to us (e.g. robotic domestic assistants, biomechatronic prostheses and orthoses), new requirements arise for a safer, more effective, and easier interaction with humans. It is not just a matter of producing environmentally suitable machines (e.g. the machines should not be noisy or polluting). It is, in general, a matter of having machines that are dependable, light, simple, and, somehow, easy to design and optimize for a specific task. Many actuators, including electric motors, transform electric energy into mechanical energy through an electromagnetic field. This intermediate step in energy transduction causes a bottleneck because of the limit in the maximum energy density associated with an electromagnetic field. Low energy density may negatively reflect on power density, causing actuators and, ultimately, the machines implementing them, to be heavy and bulky. Conversely, in fluidic actuators (i.e. hydraulic or pneumatic) energy is stored as fluid pressure and, therefore, there is no theoretical limit for energy density. Nevertheless, the need for external devices, required to transfer energy to the fluid, such as pumps and compressors, makes actuators of this type equally heavy and bulky. As an example, Kazerooni [1] developed a state-of-the-art pneumatic exoskeleton where the compressor, powered by an internal combustion engine, is carried on the user's back and, therefore, such a solution is not suitable for operating close to people suffering from physical disabilities.

Mechanical energy is available whenever pressure and volume changes are produced within the fluid. This is evident if the fluid is a liquid and gas is generated inside it. In this case, a large volume or pressure increase can take place. This result can be achieved by means of different processes, which can be grouped in two main classes: (1) phase transition (liquid→vapour) and (2) gas formation by chemical/electrochemical reactions. The processes can be further classified according to whether the enthalpy of the liquid is more or less than the enthalpy of the gaseous products. In the former case, the liquid is called a propellant. As an example of the latter case, in 2005 Accoto et al. [2] demonstrated that pressure could be generated in loco inside deformable structures to produce rotation, powering an electrolytic solution with an adequate current intensity. In this case the work performed by the actuator is provided by

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electricity, since no energy release occurs in the liquid.

As it regards propellants, hydrogen peroxide (H_2O_2) has been used since WWII for military and aerospace applications. It has been considered as an alternative to hydrazine, a high energy density propellant, which is carcinogenic and difficult to handle. Conversely H_2O_2, shows many characteristics that make it a good candidate for actuation purposes: it is quite stable and low reactive at standard conditions (mostly for low-concentration solutions), nontoxic, easy to handle and store. H_2O_2 quickly reacts over metal-based catalysts (such as Ag or Pt) to release oxygen and water, which can be sent to special pneumatic pistons. Striking results in controlling machines using H_2O_2 as propellant have been presented by Michael Goldfarb and collaborators at Vanderbilt University [3]. H_2O_2 decomposition is strongly exothermic, which makes this chemical appealing as a propellant. On the other hand, this clearly poses problems in terms of temperature control. Reaction temperature depends on different factors, such as reactants and catalyst amounts and pH.

In this work a kinetic and thermodynamic model of H_2O_2 metal catalyzed decomposition reaction is provided and validated by tests conducted on strongly alkaline H_2O_2 solution with solid tin as catalyst. The matching between model and experimental data is then discussed and used to completely characterize reaction's kinetic behaviour and actuation's performances.

II. H_2O_2 Decomposition Reaction

H_2O_2 decomposes, according to the following reaction:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \uparrow \tag{1}$$

yielding non-harmful products (water and gaseous oxygen).

The reaction is strongly exothermic ($\Delta h_{rx} = -98\,\mathrm{kJ \cdot mol^{-1}}$ at 20°C) and in adiabatic conditions may result in gas expansion and water vaporization.

At room temperature, almost no decomposition occurs but several metal catalysts based on Ag, Cu, Fe, Mn, Ni, Pt and their oxides catalyze the H_2O_2 decomposition. Earlier studies [4], suggest that this reaction follows a first order kinetics respect to peroxide concentration, that is, the reaction rate per unit catalyst surface, r $[\mathrm{mol \cdot s^{-1} \cdot m^{-2}}]$, is expressed by:

$$r = k\,[H_2O_2] = k_0 \exp\left(-\frac{E_a}{RT}\right)[H_2O_2] \tag{2}$$

where k is the first order kinetic constant and $[H_2O_2]$ is hydrogen peroxide istantaneous concentration in the solution; the kinetic constant, according to the Arrhenius equation, is a function of temperature T, via the parameters k_0 and E_a (the activation energy), which are catalyst-dependent.

High-concentration H_2O_2 solutions seem to be promising in terms of energy contents: a 70% H_2O_2 solution has an energy density of $2\,\mathrm{MJ \cdot kg^{-1}}$ and the gas phase produced can be successfully exploited as a pneumatic actuator propellant. The main drawback, however, is that the reaction is accompained by a large tempetature rise (the adiabatic decomposition temperature for a 70% solution is about 230°C) up to values that are not suitable in systems that have to work in intimate contact with a human operator. In order to successfully apply H_2O_2 propellant capabilities in the field of rehabilitative robotics, it is possible to act on other factors that can affect reaction kinetics, such as pH of liquid mixture. In a study on H_2O_2 decomposition in an alkaline environment, Abbot et al. [5] demonstrated that, in solutions with pH in the range $9 - 13$, the reaction occurs at 20°C even in absence of solid catalysts and it is as faster as pH increases. One of the reaction mechanisms proposed by Duke et al. [6] in order to explain this effect in alkaline media, assumes a bimolecular process, involving the perhydroxy anion:

$$OH^- + H_2O_2 \rightarrow HO_2^- + H_2O \tag{3}$$

$$H_2O_2 + HO_2^- \rightarrow HO^- + H_2O + O_2 \tag{4}$$

The formation of the HO_2^- intermediate is the rate-controlling step and it is promoted by OH^- in the solution. In any case, much higher reaction rates are observed if a solid catalyst is present. The use of an alkaline reaction environment in conjunction with heterogeneous metal-based catalysis may allow to obtain adequate volumes of O_2 in a short time, starting from low-concentration H_2O_2 solutions. In this work the effectiveness of solid tin as low-cost catalyst in basic pH solution is demonstrated, to obtain a fast H_2O_2 decomposition at acceptable temperature.

III. Experimental

In order to characterize H_2O_2 low-temperature, tin-catalyzed decomposition reaction in an alkaline environment, both in terms of kinetics (activation energy and rate of gas evolution) and actuation performances, two different sets of experiments were performed: in the first set, the reaction was carried out in an open constant-volume reactor and the gas produced was collected and measured; in the second set, the reaction was carried out in a closed constant-volume chamber and the gas pressure was registered. The test-benches are depicted in Figure 1.

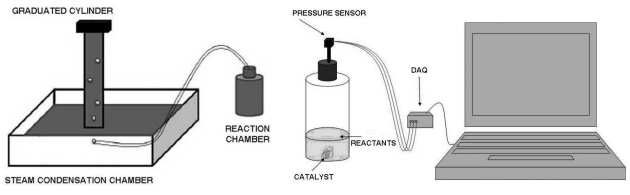

Figure 1: Schema of experimental setups: (a) open (b) closed reactor

In open reactor tests (Figure 1a), 10 ml of an aqueous H_2O_2 solution of known concentration were put in a reaction chamber with a volume of 500 ml. A mass of 0.1 mg of NaOH was added to the liquid mixture, obtaining a

$\mathrm{pH} = 13.4$ solution. The catalyst ($1\,\mathrm{mm}$ diameter tin wires, variable in number and lenght) was pre-washed with ethanol and water, in order to dissolve impurities, then wires were inserted into the reaction chamber, starting the decomposition reaction. A plastic catheter was used to direct the gas outlet to a collection chamber constituted of a closed cylinder filled with water. The gas entered the collection chamber by bubbling in a bath of ambient temperature water, so that steam was virtually completely removed and only oxygen was eventually collected and its volume measured. The levels of the collection chamber and water bath were chosen in order to keep the collected gas at atmosferic pressure ($\pm 3\%$); furthermore, it may be assumed that the collected gas is at room temperature. Elapsed time at regular collected oxygen volume-intervals of $25\,\mathrm{ml}$ was registered.

Three different experiments were carried out varying the initial H_2O_2 concentration and catalyst surface (see Table I). Results are shown in Figure 2.

Table I: H_2O_2 concentration and catalyst surface area in open reactor reactor test (solution volume: $10\,\mathrm{ml}$)

Test	1	2	3
$[H_2O_2]\,\%\mathrm{w}$	10.6	12.7	12.7
$S_{cat}\,[cm^2]$	7.8	7.8	15.7

Since H_2O_2 tin-catalyzed decomposition reaction in an alkaline solution shows characteristic times of gas evolution short enough to be considered for pneumatic actuation, the second set of experiments was aimed at verifying whether the pressures exherted by the gas are compatible with actuation requirements. In all these experiments, a $100\,\mathrm{ml}$ of $12.7\%\,H_2O_2$ solution containing $1\,\mathrm{g}$ of NaOH was used, while the catalyst surface was varied (see Table II). Again, the reaction was conducted in a $500\,\mathrm{ml}$ reactor. After the reaction start, the pressure in the reactor was continuously measured with a differential pressure sensor (Honeywell mod P-30-P range 150 psid) and the pressure time-course was recorded with DAQ (NI model USB-6009). Since the maximum pressure allowed in the experimental set-up was 2.5 atm, each time the pressure approached this value, a valve was opened until it dropped to 1 atm. Results are shown in Figure 4.

Table II: H_2O_2 concentration and catalyst surface area in closed reactor reactor test (solution volume: $100\,\mathrm{ml}$)

Test	4	5	6
$[H_2O_2]\,\%\mathrm{w}$	12.7	12.7	12.7
$S_{cat}\,[cm^2]$	7.8	23.7	78

IV. Reaction Model

In order to analyze the preliminary results obtained with the open reactor tests, a mathematical model was developed. The model was also matched against the experimental data in order to obtain the catalyst-dependent parameters k_0 and E_a, that are needed to calculate the tin-catalyzed decomposition rate. The main assumptions of the model are: 1) negligible oxygen absorption in the liquid phase and H_2O_2 vaporization; 2) ideality of the H_2O_2-H_2O liquid mixture; 3) uniform temperature in the liquid phase; 4) negligible conduction heat losses trough the reactor walls.

The model includes unsteady mass and energy balances applied to the liquid phase in the reactor. For the three compounds involved in the reaction, mass balances are given by:

$$\frac{dn_{H_2O_2}}{dt} = -\mathcal{R} \tag{5}$$

$$\frac{dn_{H_2O}}{dt} = \mathcal{R} - F_{H_2O} \tag{6}$$

$$F_{O_2} = \frac{\mathcal{R}}{2} \tag{7}$$

where n_i are the number of moles of compound i in the liquid phase, F_i is the molar flow rates of compound i leaving the liquid phase, $\mathcal{R}$ is the reaction rate $[\mathrm{mol}\cdot\mathrm{s}^{-1}]$. The energy balance is

$$\sum_{i=1}^{c} \frac{d}{dt}[h_i^L(T)\cdot n_i^L] = -\sum_{i=1}^{p} F_i h_i^V(T) \tag{8}$$

where h_i^L and h_i^V are the specific enthalpies of compound i in the liquid and vapour phase, respectively $[\mathrm{J}\cdot\mathrm{mol}^{-1}]$.

The oxygen and water molar flow rates leaving the liquid phase are bound by the water liquid-vapour equilibrium condition:

$$\frac{F_{H_2O}}{F_{H_2O}+F_{O_2}}P = \frac{n_{H_2O}}{n_{H_2O}+n_{H_2O_2}}p_w^s(T) \tag{9}$$

where P is the reactor pressure and p_w^s is the water vapour pressure.

As earlier discussed, H_2O_2 metal-catalyzed decomposition follows first-order kinetics (eq. (2)); then, the reaction rate is given by:

$$\mathcal{R} = r\cdot S = k_0\cdot\exp\left(\frac{-E_a}{RT}\right)\cdot n_{H_2O_2}\frac{S}{V_L} \tag{10}$$

where S is the effective catalyst surface and V_L is the time-dependent liquid mixture volume.

The system of Differential-Algebraic Equations (5)-(9) can be numerically solved to obtain the time course of the following variables $n_{H_2O_2}$, n_{H_2O}, F_{H_2O}, F_{O_2} and T.

Finally the total amount of oxygen collected, $n_{O_2}^{out}$, is given by:

$$n_{O_2}^{out}(t) = \int_0^t F_{O_2}dt'$$

V. Results and Discussion

A. Open reactor experiments

The time-course of the collected oxygen volume shows a sigmoidal shape (Figure 2), respondent to three different process phases. Initially, immediately after catalyst insertion, the reaction rate is slow because of the low temperature (Figure 3); subsequently, the heat produced by the reaction

raises the temperature and the reaction becomes very fast: the residual amount of H_2O_2 decomposes in few seconds, the volume of released oxygen increases rapidly and almost linearly. Finally, when the decomposition is almost complete and H_2O_2 concentration is very low, the reaction slows down again.

The effect of initial H_2O_2 concentration can be observed by comparing results of test 1 (Figure 2a) with experiments 2 and 3 (Figure 2b). It is clear that in the case of lower H_2O_2 initial concentration the reaction rate is lower: more specifically, in order to produce $350\,\mathrm{ml}$ of oxygen, $460\,\mathrm{s}$ were needed in experiment 1 and $300\,\mathrm{s}$ in experiment 2. Furthermore, since all the experiments were carried out with the same initial liquid volume, a higher initial H_2O_2 concentration corresponds to a higher initial H_2O_2 amount and, therefore, to a higher maximum oxygen volume that can be produced. This maximum value, that can be calculated from reaction stoichiometry, is reported as an horizontal line in Figure 2a and 2b for each data set.

By comparing the results of data sets 2 and 3, reported in Figure 2b, it is possible to observe the effect of catalyst surface on the process: in test 3, in which contact surface has been doubled respect to test 2 while keeping the initial H_2O_2 concentration constant, $25\,\mathrm{ml}$ of oxygen were produced after $105\,\mathrm{s}$; in the test 2, $166\,\mathrm{s}$ are nedeed to produce an equal amount of oxygen. It is worth nothing that, in these preliminary experiments, the catalyst surface area is always low. Considerably larger surface area can be obtained using high-porosity solids or structured catalysts as metallic foams.

The kinetic model, discussed in section IV, was fit to experimental data set 1 using E_a and k_0, which were unknown for the catalyst used, as adjustable parameters. At this aim, a numerical optimization procedure was carried out by using MATLAB (The Mathworks, inc.). The optimal values found for the parameters are $E_a = 61\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ and $k_0 = 3.5\cdot 10^5\,\mathrm{m}\cdot\mathrm{s}^{-1}$. The results of the fitting are presented in Figure 2a, where the calculated curve (solid line) is superimposed to the corresponding experimental data. It can be seen that model results are in good agreement with experimental data, confirming that the model proposed is suitable to describe the reacting system.

The value obtained for the activation energy E_a is very close to that reported in literature [7] for other non-specific metal-based catalysts, which confirms tin good performances as catalyst for H_2O_2 decomposition reaction.

The set of parameters obtained by fitting data of experiment 1 were subsequently used to predict the effect of H_2O_2 concentration and catalyst surface area on the process kinetics; the model prediction are compared with the experimental data in Figure 2b. The satisfactory agreement between the model prediction and experimental data suggests that the model has predictive capabilities that could be useful in the design of the H_2O_2-based actuation systems. It can be noted that the major discrepancies between experimental data and predicted curves are observed at longer times. This could be due, for instance, to the heat lost through the reactor walls, that is not accounted for in the model and that becomes more significant as time increases.

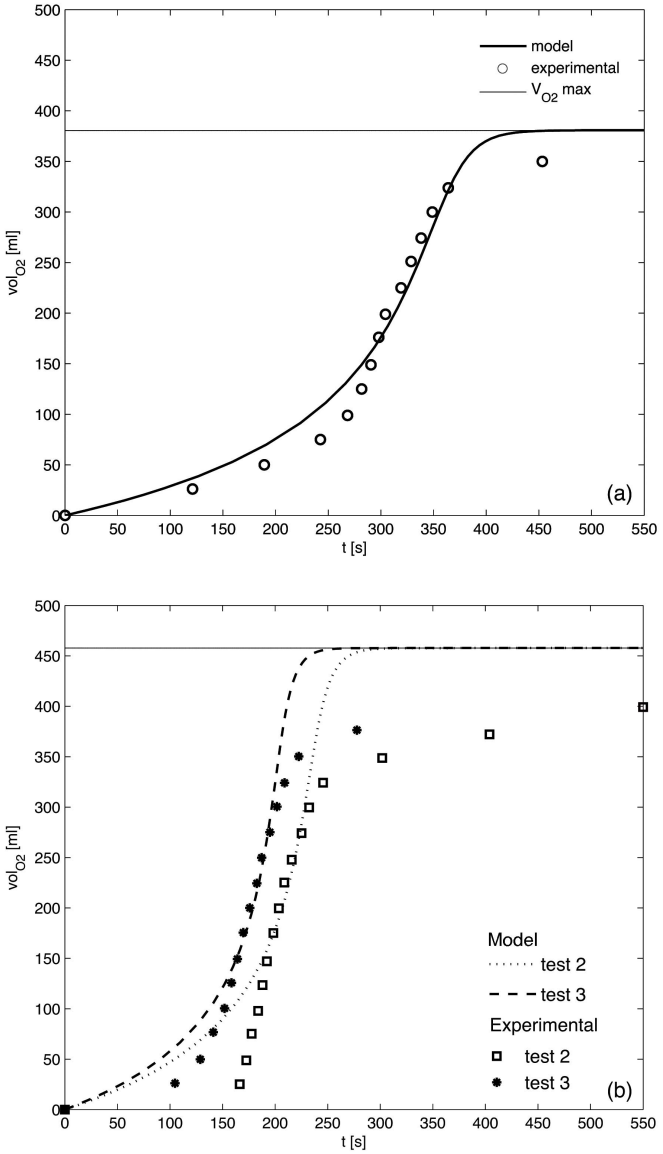

Figure 2: Oxygen production time-course in the open reactor experiments. (a) test 1, (b) test 2 and 3

Finally, Figure 3 shows plots of reacting mixture temperature Vs. time, as computed by the model. In all cases, temperature rapidly increases, following the reaction extent. Obviously, the maximum temperature that can be reached depends on the initial H_2O_2 amount and, for the conditions considered in this paper, it is slightly more than $90°\mathrm{C}$. Such a maximum temperature is considerably lower than those reached at the end of higher-concentration H_2O_2 solutions decomposition and it can be considered acceptable for the intended applications, in terms of safety of materials and, with proper thermal insulation, operators.

B. Closed reactor experiments

Figure 4 shows the pressure time-courses in the closed reactor tests. In the reported plots, it is possible to identify

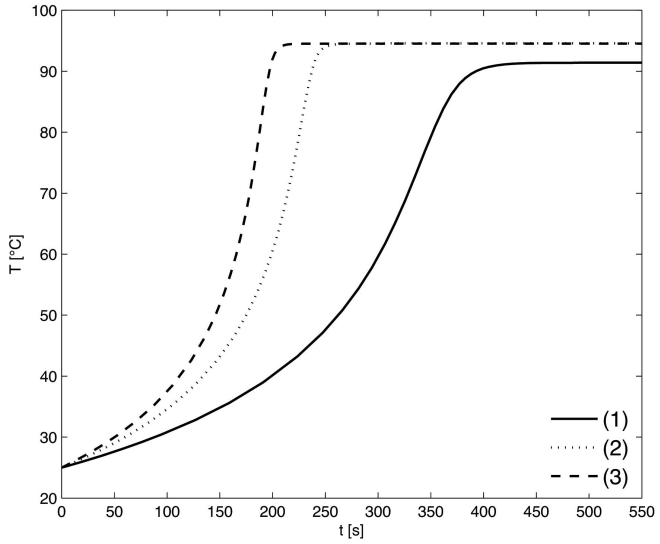

Figure 3: Calculated temperature time-course in the open reactor experiments. Experimental conditions: see Table I

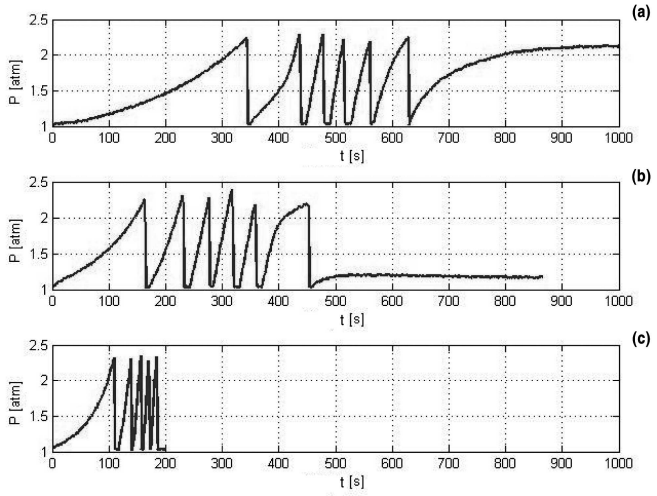

Figure 4: Pressure of the gas in the reaction chamber. Experimental conditions: see Table II

an initial phase of progressive pressure rising, followed by a series of sawtooth-like cycles (due to cyclic gas spill-out) and then a final saturation zone. The effect of catalyst surface on gas pressure evolution rate is shown in Figure 4b, where results of test 5 are reported. Owing to the larger contact area ($23.7\,\mathrm{cm}^2$), the reaction is faster than in experiment 4, as expected, and the first peak is reached in a shorter time ($150\,\mathrm{s}$ Vs. $350\,\mathrm{s}$). Furthermore, with a ten-fold increase in the catalyst surface, as in test 6 respect to test 4, the enhancement of reaction kinetics is much more evident: during test 6, the first gas spill-out had to be performed only after $100\,\mathrm{s}$, followed by four other pressure peaks in a time span of $100\,\mathrm{s}$, each with higher slopes if compared to the other experiments. On the other hand, with the same initial amount of H_2O_2, the maximum number of cycles decreased as the catalyst area was increased: the faster the raction rate, the faster the propellant is completely decomposed. This is an important point to be accounted for in the design of H_2O_2-based actuators, because the propellant make-up frequency is a relevant performance parameter when such devices must be applied to rehabilitative and assistive robotics.

VI. Conclusions

Power supply systems still pose major issues in several biorobotic applications where the machine is in close proximity to the human body. Monopropellant-based actuators are promising alternatives to hydraulic and pneumatic actuators, since they directly convert chemical energy into mechanical energy, with no need for bulky accessories such as pumps and compressors. In particular, H_2O_2 has been successfully used in robotics. Anyhow, the energy released during the decomposition reaction is often associated with intolerably high temperatures, which increase with the propellant concentration in the reacting mixture. Anyhow, H_2O_2 concentration can be reduced, without affecting gas production rate, if an alkaline solution is used.

In this work an experimental and theoretical investigation on low-concentration H_2O_2 tin-catalyzed decomposition is presented.

This process is intended to operate at acceptable temperatures, still obtaining satisfactory actuation performances, by combining the advantages of metal-based catalysts and alkaline reaction environment. Furthermore it is worth nothing that a simple on-off control strategy can be obtained by catalyst insertion and extraction in the liquid phase.

A model, based on a thermodynamic and kinetic analysis, is described. The model was fit to a set of experimental data obtained in an open, constant-volume reactor, thus setting the optimal values of reaction kinetic parameters.

The predictive capability of the model was subsequently tested on different sets of experimental data, obtaining satisfactory results. A second set of experimental tests was carried out in a closed, constant-volume reactor, in order to evaluate the pressures that can be reached using the described decomposition reaction. Both model and experimental data confirm that the proposed process seems to be promising, because gas is produced starting from a low-concentration monopropellant solution, avoiding the risk of high temperature rise.

The model provides useful starting point in the design of propellant based actuators, because it allows estimating the effect of catalyst surface on gas production rate, as well as the expected final temperature.

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