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POWER SYSTEMS AND POWER ELECTRONICS

Solar chargers based on new dye-based photovoltaic modules and new supercapacitors

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Abstract. Electricity storage is one of the best-known methods of balancing the energy supply and demand at a given moment. The article presents an innovative solution for the construction of an electric energy storage device obtained from an innovative photovoltaic panel made of new dye-based photovoltaic modules and newly developed supercapacitors – which can be used as an emergency power source. In the paper, for the first time, we focused on the successful paring of new dye-sensitized solar cell (DSSC) with novel supercapacitors. In the first step, a microprocessor stand was constructed using Artificial Intelligence algorithms to control the parameters of the environment, as well as the solar charger composed of six DSSC cells with the dimensions of 100×100 mm and 126 CR2032 coin cells with a total capacitance of 60 F containing redox-active aqueous electrolyte. It was proven that the solar charger store enough energy to power, i.e. SOS transmitter or igniters, using a 5 V signal.

Key words: dye-sensitized solar cell; supercapacitor; redox-active electrolyte; current source, energy storage system; Artificial Intelligence.

1. INTRODUCTION

Currently, the commercial market is flooded with innovative solutions [1–3] of devices for obtaining and storing energy from the sun. The most widely used are energy storage based on batteries (electrochemical cells) and hybrid systems, in which supercapacitors are additionally used as a buffer for a high-current source [4–6]. The electrical solutions of the warehouse determine the receivers. Hence, an increasing number of recent developments of highly specialized warehouses designed for specific purposes appear on the commercial market [7, 8].

A dynamically growing supercapacitor technology is a response to current market demands for sustainable and reliable energy reservoirs for applications requiring a high, but also uninterrupted power supply. The specific energy of typical purely capacitive (double layer-type) supercapacitors is, however, rather low in comparison to electrochemical (battery) cells. Therefore, a zinc iodide-redox flow battery-inspired (RFB) concept of hybridization was a serious breakthrough [9]. Introducing a neutral redox-active alkali metal iodide electrolyte enables even up to 10 times increase in the specific energy in comparison to the conventional acidic or alkali aqueous systems. Additionally, and in contrast to RFB, such a redox electrolyte-aided hybrid supercapacitor operates under stationary conditions facilitating cost-efficient and small design, as well as more versatile applications.

This paper presents an innovative approach to the construction of a solar charger using the latest developments of key elements (subassemblies) of Polish companies and research institutions. The work was conducted under the Techmatstrateg project as part of the task entitled: "Efficient and lightweight power systems consisting of a solar cell and a supercapacitor for special applications", the aim of which was to construct a solar charger and test it for various types of connections between solar cells and a supercapacitor. The article also presents the tests of the finished device in laboratory conditions with the use of a microprocessor measuring system that improves the efficiency of measurements. It is a tribute to the digital transformation of AI (Artificial Intelligence) measurement processes that bring immeasurable benefits in terms of saving time and minimizing errors made during tedious measurements [10, 11]. The obtained results are presented in the form of charging, discharging, and recharging characteristics. To achieve the intended goals, a dye cell module with a total area of 100 cm^2 filled with gel electrolyte was used, with an efficiency almost identical to that of the liquid electrolyte. Carefully previously optimized [3] hybrid supercapacitors utilizing the potassium iodide active electrolyte in the form of coin cells were used as the energy storage unit for our new photovoltaic panels for the first time. Noteworthy, the high specific energy of the supercapac-

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itor (17 Wh kg^{-1}) facilitated reducing the number of the coin cells building the module by a factor of ca. 2 in comparison to the conventional double layer-type counterpart with the same target capacitance.

2. MATERIALS AND METHODS

2.1. Construction of dye-sensitized solar cell

The initial stage of designing the architecture of dye cells (DSSC) was the selection of optimal physicochemical properties of the material to ensure the achievement of parameters that guarantee the efficient operation of third-generation cells. As a result of the research, the architecture of photovoltaic modules with total dimensions of 100×100 mm consisting of six or eight individual cells connected in series was designed (Fig. 1).

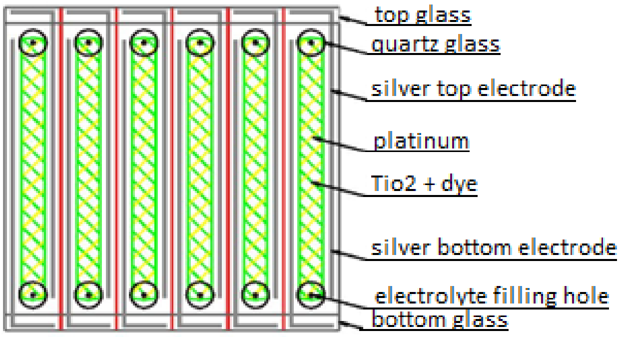

Fig. 1. Architecture of the DSSC module with dimensions of 100×100 mm

The cells were prepared on glass covered with a conductive FTO layer (SnO_2:F, TEC A7, 6–8 Ω/cm). The photoanode was FTO glass, additionally covered with an approximately 30-nanometer layer of TiO_2 constituting the electron-blocking layer. The layer was prepared by the method of magnetron sputtering.

A MiniSpectros ™system (Kurt J. Lesker Company Ltd.) with 99.99% pure TiO_2 target was used for this purpose. In the next step, the screen printing method was used (semi-automatic screen printer, WJATECH), which was covered with a mesoporous layer of titanium (IV) oxide nanoparticles. Two pastes containing different sizes of nanoparticles were used: smaller < 25 nm (18NR-T, GreatCell Solar) and larger < 450 nm (18NR-AO, GreatCell Solar). The first one was printed three times and was a dye-adsorbing layer. The second one was printed once, and its role was to adsorb the dye and scatter light in the photoanode. The thickness of the obtained layer was approx. 13 µm. The dyeing process, i.e. attaching highly light-absorbing molecules to TiO_2 nanoparticles, was conducted for 24 hours in a 4×10^{-4} M dye solution N719 (B2-N719, DyeSol) dissolved in ethyl alcohol (99.8%, Honeywell). The photocathode was made of FTO glass coated with platinum nanoparticles (PT-106, 3D-nano), which performs a catalytic function in redox reactions in the electrolyte. For this purpose, the screen printing method was also used. The photoanode and photocathode additionally contained silver traces drawn from a paste (SilverCon) located at a short distance parallel to the layers of titanium (IV) oxide and platinum. Their task was to collect the generated charge carriers and effectively transfer them to the external electrodes, thus preventing recombination, i.e. disappearance, in the SnO_2:F structure. The glasses obtained in this way were joined in the lamination process (P.Energy Laminator) using a laminating foil (Surlyn®DuPont ™) with a thickness of 60 µm. The electrical contact between the electrodes was ensured by forcing the gel electrolyte obtained in WITI into the cell chamber, selected as the most effective [12].

DSSC modules with dimensions of 100×100 mm were made, containing 6 cells with an active photosensitive field of 5.6 cm^2 or 8 cells with an active photosensitive field of 7.36 cm^2 connected in series. The cells were placed on one FTO glass. The electrical separation of individual cells was performed by laser ablation of the conductive SnO_2: F coating with a laser $\lambda = 532$ nm, thus obtaining 6 or 8 separate sections, respectively. The use of six or eight DSSC cells in the module facilitated the sufficient separation of the individual components of the photovoltaic device. The antisymmetric arrangement of the electrodes on both glasses allowed one to use only one laminating foil (60 µm) and in the case of the eight-fire module, it was necessary to use two laminating foils (2×60 µm). The modules were secured by sticking additional thin glass with a thickness of 1 mm with epoxy resin (Epidian®Deco) to protect the electrical cables against mechanical damage. Additionally, a thin silver coating is placed on the top glass. Its function was to reflect the light not absorbed by the cell towards the active layer, which increased the efficiency of using the incident radiation.

2.2. Construction of supercapacitors

The research used a hybrid supercapacitor with increased capacitance and specific energy in relation to classic electrical double-layer supercapacitors. The charge in the developed module is stored as a result of the coupled mechanism of physical adsorption of electrolyte ions on the surface of porous activated carbon electrodes and as a result of fast (surface-type) oxidation and reduction reactions of the redox mediator ($I^-/I_2/I_n^-$) present in the solution [3,12]. The module consisted of 126 CR2032 coin cells placed on the PCBs. Each cell was a system of two in series connected supercapacitors, which allowed to increase its maximum voltage from 1.5 to 3 V. The supercapacitor electrodes were made of activated carbon YP-80 F (Kuraray, Japan) with a specific S_{BET} surface area of 2607 m^2/g and micro- (< 2 nm) and mesopore (> 2 nm) volume of 0.82 and 0.6 cm^3g^{-1}, respectively. The electrodes, in the form of disks with a geometric area of 1.77 cm^2 and a thickness of 200 µm, impregnated with an aqueous electrolyte (0.5 mol/dm^3 KI/0.5 mol/dm^{-3} K_2SO_4), were separated by a Celgard 3501 polypropylene separator and closed in a coin casing under the pressure of 2000 psi (Fig. 2a–b). The capacitance and energy of each supercapacitor were equal to 0.5 F and 0.62 mWh, respectively. A representative example of the charge-discharge characteristics of the individual coin cells recorded under voltammetric conditions can be seen in Fig. 2c.

Two final supercapacitor modules with a target capacitance of 60 F were constructed in the research. As seen in Fig. 2d, the

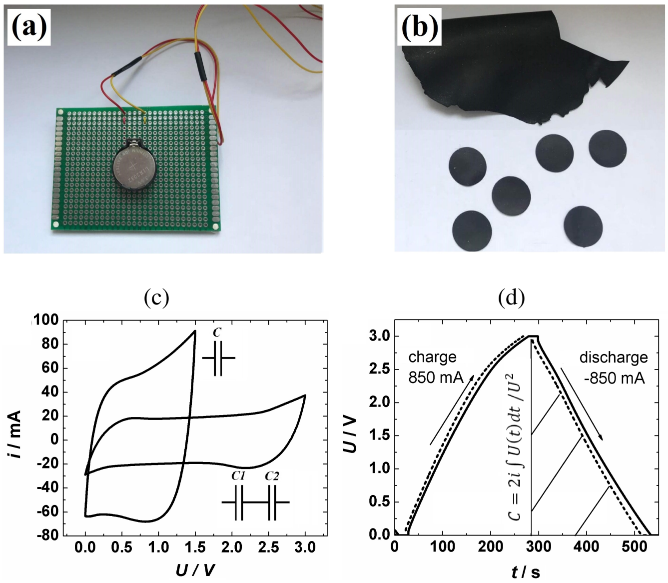

Fig. 2. (a) A supercapacitor in a CR2032 housing placed on a PCB in a pocket for diagnostic tests, (b) Supercapacitor electrodes cut from the YP-80F carbon sheet, (c) Voltammetric curves ($v = 50$ mV s^{-1}) of a supercapacitor ($U = 1.5$ V) and two serially connected supercapacitors ($U = 3$ V) within one coin housing, (d) Galvanostatic curve of complete modules ($i = 850$ mA)

prototypes exhibited almost identical constant current charge-discharge characteristics which shows a high reproducibility of the presented approach. Additionally, the equivalent series resistance of the modules, Rs measured by the EIS method with a 4-point connection was only ca. 24 mΩ (at 3.2 kHz). The additional contribution to the charge transfer resistance, the R_{CT} was equal to 50 mΩ (at 19.7 Hz). The device, therefore, meets the criteria of a high-power system.

2.3. Construction of solar charger

During preliminary work on the design of a solar charger based on new dye photovoltaic modules developed by ML System [12] and new supercapacitors developed by Warsaw University (Fig. 3), the current-voltage characteristics of dye modules (Fig. 4), together with charging and discharge characteristics of new supercapacitors (Fig. 5) were measured. After analyzing the parameters [13] of the tested modules, preliminary

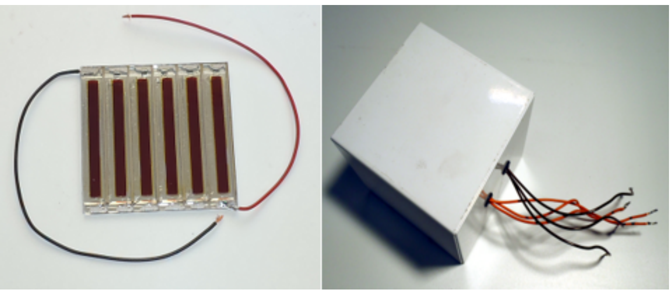

Fig. 3. View of the B2 photovoltaic dye module with a photosensitive field area of 33.6 cm^2 and a new supercapacitor with a capacitance of $C_{SC} = 60$ F, rated operating voltage $U_C = 3$ V and series resistance $R_S = 106$ mΩ

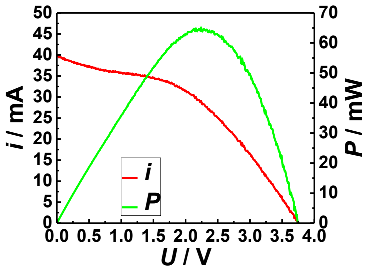

Fig. 4. Current-voltage characteristics of a dye module with a photosensitive field area of 33.6 cm^2 ($V_{OC} = 3.8$ V, $I_{SC} = 25.9$ mA, $V_{\max} = 1.6$ V, $I_{\max} = 12.2$ mA, $P_{\max} = 19.7$ mW, $R_{so} = 207$ Ω, $R_{sho} = 96$ Ω, $\eta = 0.8\%$, $FF = 0.2$)

measurements allowed us to determine the following parameters that characterize the charger:

1) charging current of the new supercapacitor, which is the output current from a dye photovoltaic cell;
2) the operating voltage of the new USC supercapacitor, which was limited to 2.5 V for safety reasons.

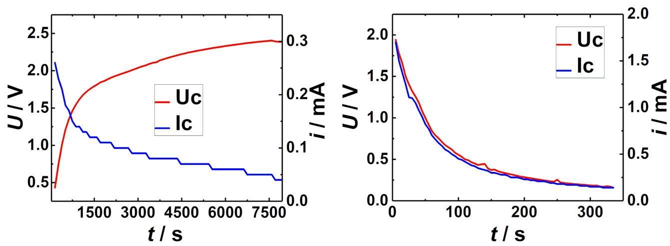

Fig. 5. Charge and discharge characteristics of a new supercapacitor ($C_{SC} = 60$ F)

Figure 6 shows a view of the constructed model of a solar charger. Additional elements installed in the charger model are:

- control switch (1) for checking whether the voltage on the supercapacitor during charging exceeded 2V;
- LED (2), which is used to signal the excess voltage of 2V on the supercapacitor;
- measuring socket (3) for connecting the charger model to the microprocessor measuring system;
- the output socket (4) for connecting the load.

Under the adopted construction philosophy (minimum number of changes in the mechanical structure of components), the

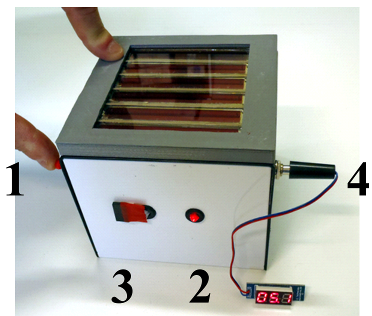

Fig. 6. A model of a constructed solar charger based on dye-based photovoltaic modules and new supercapacitors

functional model of a solar charger based on new photovoltaic dye modules was divided into individual modules (subassemblies):

- dye photovoltaic module;
- a frame of a dye photovoltaic module printed on a 3D printer from PLA filament;
- a new supercapacitor with a capacity of $C_{SC} = 60$ F and a rated operating voltage of $U_C = 3$ V;
- a replica of the supercapacitor upper case.

According to the above division, a dye-cell module was mounted in the frame, which was attached to the replica of the upper case of the new supercapacitor, which was then attached instead of the cover part of the original supercapacitor from UW. The currents and times of charging, discharging, and recharging the charger were the result of measurements already carried out on the finished model.

2.4. Methods

The supercapacitor module was constructed as described elsewhere [3]: construction of a solar charger consisted of three printed circuit boards with space for parallel connected CR2032 coin cell holders. Each coin cell was fabricated using a manual crimping machine (GN-CC20, Gelon Lib, Shandong, China) and contained two series-connected supercapacitors separated by a stainless steel spacer. The area and thickness of each electrode were equal to 1.77 cm^2 and 200 ± 10 μm, respectively. The total activated carbon mass loading in the cell was equal to 32.4 ± 0.2 mg cm^{-2}. The total number of CR2032 cells in the module was equal to 126.

The SS150AAA solar radiation simulator coupled with the $I-V$ Tracer SS IV CT-02 system and Keithley Source meter SM2401 was used for measuring the $I-V$ characteristic of dye-sensitized solar cells.

The microprocessor measuring system was set up to acquire simultaneously current-voltage characteristics of the photovoltaic panel, DC/DC converter, and supercapacitor module together with environmental parameters, such as pressure, temperature, humidity, and illumination. Artificial Intelligence was implemented for data fusion from different measuring modules, giving a single data file.

3. DISCUSSION OF RESULTS

The tests of the constructed solar charger were conducted on a microprocessor stand for testing the parameters of functional models of solar chargers developed fully by Polish institutions and a company. The system of the current source, voltage control of a supercapacitor with a capacity of $C = 60$ F and an operating voltage of $U_C = 2.5$ V was connected to the power supply and the microprocessor meter of voltages and currents. The microprocessor meter additionally monitors the environmental conditions and the intensity of sunlight. The measuring system cyclically sends data to the PC, where the proprietary program (written in C #) (Fig. 7) is saved in the form of a text file on the HDD. The application of AI for data fusion facilitated the unification of acquired data in an organized manner, with adequate assignment of different parameters to a single timeline. This strategy facilitated precise interpretation of observed changes and its relation to external conditions that affects the crucial parameters like the effectiveness of solar panel during illumination.

Figure 8 shows the environmental conditions in the laboratory during measurements of charging the supercapacitor model from dye cells, and Fig. 9 shows the currents and voltages of charging the supercapacitor from dye cells.

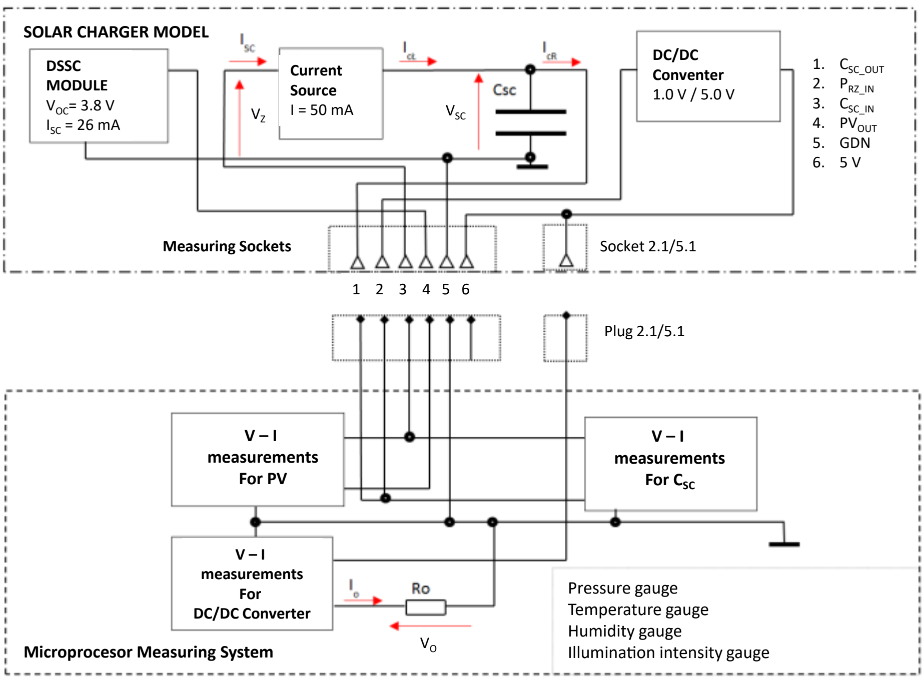

Fig. 7. Microprocessor stand for testing the parameters of functional models of solar chargers – block diagram

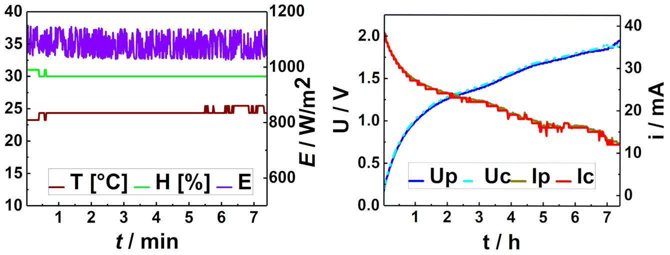

Fig. 8. Graph of environmental conditions during the measurement of charging of the supercapacitor ($C_{SC} = 60$ F) charger model from the dye photovoltaic modules

After charging the supercapacitor to the voltage $U_{SC} = 1.95$ V in the program collecting data from the microprocessor measuring system, the operating regime was switched to discharge, and the supercapacitor discharge current and voltage as well as the current and voltage at the load R_o were measured. Then, the discharge characteristics were plotted as shown in Fig. 9.

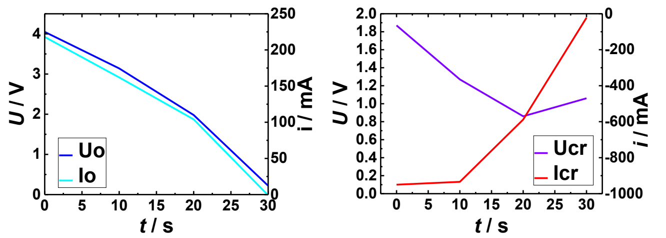

Fig. 9. Graphs of discharge of a model of a solar charger ($C_{SC} = 60$ F)

After the supercapacitor was discharged to the voltage level on it $U_{SC} = 1$ V, the work regime in the program was switched to charging and the current and voltage of the supercapacitor charging were measured. Then, the boost characteristics were plotted and shown in Fig. 10a. Figure 10b shows the environmental conditions in the laboratory during measurements of charging the supercapacitor charger model from dye cells.

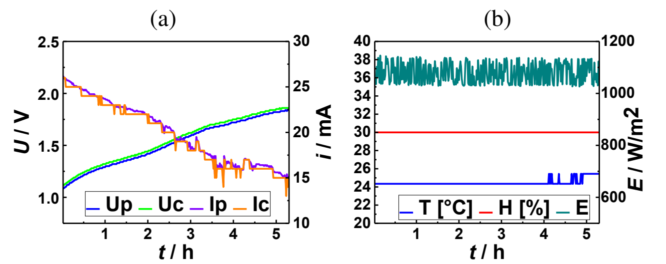

Fig. 10. (a) Graph of the boost of the solar charger model, (b) graph of the environmental conditions during the measurement of the boost of the solar charger model

Based on the obtained test results and charging, discharging, and recharging charts of the solar charger model, the electric parameters of the charger were obtained, which are summarized in Table 1.

Table 1
Electrical parameters of the constructed solar charger

Parameter	Symbol	Value for solar charger
The voltage of the supercapacitor pack	U_{SC}	1.8 V
The nominal capacity of the supercapacitor pack	C_{SC}	60 F
The theoretical amount of stored energy	W	0.027 Wh
Time of the first charge	t_n	7 h 24 min
System efficiency during the first charging of the supercapacitor pack	η_r	0.50
Possible energy recovery	W_{dl}	0.005 Wh
Voltage value for supercapacitor pack under load = 2.4 Ω, after t_r	U_{obc}	1.0 V
Discharge time to $U_{SC} = 1$ V	t_r	22 s
Energy applied to supercapacitors during recharge	E_{sc}	0.003 Wh
Time of recharge	t_n	5 h 30 min
Systems efficiency during the recharging	η_d	0.6

4. CONCLUSIONS

The made model of a solar charger based on new dye photovoltaic modules and new supercapacitors was equipped with a DC/DC 1 V/5 V 1 A converter enabling the connection of current receivers powered by 5 V DC. The obtained receiver power time of 22 seconds can be considered satisfactory in some applications, such as the emergency power supply of the SOS transmitter or igniters.

Nevertheless, it is an example of the possibilities of searching for new solutions in the field of innovative energy storage. Currently, there is no similar solution presenting a combination of DSSC and supercapacitors at such high technology readiness level. Therefore, it is difficult to compare directly its parameters. However, before future commercialization, an optimization process needs to be performed to improve the construction i.e. of the supercapacitor module to reduce its bulk size.

The paper uses knowledge in the field of new AI technologies in the area of computer-assisted measurement automation of data fusion, which generated new fields of possible innovative solutions and cooperation platforms between individual research units.

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