1	Experimental inv	estigation	of	sta	rting-up), energy-saving	g, and
2	emission-reducing	performance	ces	of	hybrid	supercapacitor	energy
3	storage systems for	automobiles					

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14 ABSTRACT

15 Improvements in engine starting-up performance, such as reducing fuel 16 consumption and exhaust emission pollution during the startup process, are very vital 17 to achieve the national development goal of carbon peaking and carbon neutrality. Hybrid supercapacitor (HSC) energy storage systems containing batteries and 18 19 supercapacitors (SCs) are considered promising energy storage strategies to 20 compensate for the disadvantages of a single energy storage technology. In this paper, 21 two kinds of novel 12 V/50 Ah and 12 V/70 Ah module-level energy storage systems 22 were first composed of cell-level 3.6 V/2200 F HSCs were designed. Analysis on 23 their fundamental electrochemical properties under room temperature conditions was also performed. Four different types of energy storage systems composed of 12 V/70 24

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Ah lithium iron phosphate (LFP) batteries, 12 V/70 Ah valve-regulated lead-acid 29 30 (VRLA) batteries, and the aforementioned HSCs were then employed to compare 31 their starting energy, energy-saving, and emission-reduction characteristics. 32 Additionally, the 12 V/70 Ah HSC module saved 7.82%, 3.18%, and 1.65% of fuel as compared to the 12 V/70 Ah VRLA, 12 V/70 Ah LFP, and 12 V/50 Ah HSC modules, 33 34 respectively, demonstrating its superior fuel economy property. Simultaneously, the 35 volume concentration of HC and CO emission in the startup process are 12.7% and 36 13.2% lower than that average of the other three modules, respectively, which shows a good exhaust emission reduction effect. The proposed energy storage system will 37 38 provide systematic experimental data support and valuable theoretical guidance for 39 the industrialization and application of HSCs.

40 Keywords:

41 Hybrid supercapacitors, energy storage systems, starting-up, energy saving, and
42 emission reduction

43 **1. Introduction**

44 In 2020, China had a transportation carbon emission of 930 million tons. Road 45 transport accounted for 90% of total carbon emissions in the entire transportation 46 sector, which road passenger transport accounted for 42% of; furthermore, 90% of 47 that came from passenger cars alone [1-3]. This also causes a large amount of fuel 48 consumption, among which, insufficient fuel combustion leads to a series of exhaust 49 emission pollution [4]. Hence, it is particularly important to improve the performance 50 of energy-saving and emission reduction of fuel trucks during ignition. In general, 51 frequent start-up processes generate severe fuel consumption and exhaust emission 52 problems [5,6]. Additionally, traditional automotive energy storage systems, such as valve-regulated lead-acid (VRLA) batteries, exhibit excessive voltage drops during 53 54 the starting process, short service life, and poor, low-temperature starting performance 55 [7,8]. Moreover, lithium iron phosphate (LFP) batteries exhibit safety risks and other

56 shortcomings during high-temperature startups [9,10]. The hybrid supercapacitor 57 (HSC) is a novel, environmentally friendly energy storage system composed of a 58 high-rate, double-layer capacitive positive electrode and large-capacity battery-type 59 negative electrode [11-13]. It has become a research hotspot due to its high power 60 supercapacitor (SC) density and high battery energy density [14-17]. HSCs integrate 61 the energy storage mechanism of double-layer capacitors and the energy storage 62 mechanism of batteries. One pole adopts a battery-type electrode to store energy through the embedding and removal of metal ions in the electrode material lattice, 63 while the other pole adopts a double-layer capacitor electrode to store energy through 64 65 the absorption and desorption of ions on the electrode material surface [18-21]. Furthermore, current self-charging SCs [22], multi-responsive healable SCs [23] and 66 foldable quasi-solid-state SCs are also widely used in flexible wearable energy 67 storage devices [24]. These emerging SCs have high potential in the next generation 68 69 of portable electronic devices.

70 Since HSCs have a higher working potential and larger capacitance to meet the 71 starting power, they can also undergo long-term starting without charging, have fast 72 charge-discharge ability, a long cycle life, and can withstand extreme low- and high-73 temperature environmental conditions [25,26] while maintaining their small internal resistance, low self-discharge, short circuit without explosions, safety, and 74 75 environmental protection [27-29]. Consequently, HSCs are more advantageous than 76 using batteries or SCs alone as a vehicle energy storage system [30,31]. As compared to the composite power supply, it is unnecessary to use an SC in series or parallel with 77 78 a VRLA or LFP battery, thus saving space, simplifying the design, and lowering the 79 long-term cost [32-35].

HSC energy storage systems have been increasingly researched in recent years.
For example, Sun et al. [36-38] comprehensively reviewed the preparation method
and electrochemical performance of CuCo₂O₄-based HSC materials, which provided
valuable theoretical guidance for the engineering applications of HSCs. Shao et al.

[39-43] studied graphene as the anode material of lithium-ion HSCs and verified its 84 high energy and excellent high-power properties. Chen et al. [44-46] prepared nickel 85 foam-supported MnCo₂O_{4.5} porous nanowires with high-performance HSCs 86 87 electrodes, showed an impressive cyclic stability, and reviewed the progress of the application research of MgCo₂O₄-based composites in SCs. Yin et al. [47] fabricated 88 89 (Ni,Co)Se₂ nanoparticles on vertical graphene nanosheets@carbon microtubes 90 membrane electrode for HSCs exhibits excellent electrochemical performance in terms of high specific capacitance (1740 F g⁻¹ at 1 A g⁻¹), good rate capability (71.8% 91 capacitance retention at 20 A g^{-1}), and superior cycling stability (89.6% capacitance 92 93 retention after 10,000 cycles). Liu et al. [48,49] explored the engine starting 94 performance of composite energy storage systems based on SCs. Their results 95 exhibited shorted engine starting times and improved engine starting performance. Guo et al. [50,51] designed a 48 V LI ion capacitor start-stop power system, the 96 97 results of which indicated that the vehicle had very good fuel economy during startup. Yu et al. [52-55] proposed a composite power supply combining battery and SC. The 98 99 bench test showed that the composite energy storage system provided a greater 100 starting current and improved starting power compared with lead-acid batteries. 101 Zhang et al. [56-59] studied the composite energy storage system composed of lead-102 acid battery and lithium titanate battery in parallel, the results of which showed that the composite energy storage system was conducive to improving the cycle life of 103 104 lead-acid battery and optimizing energy-saving effects and emission reduction. Liu et al. [60-62] examined a new hybrid power system of 42 V vehicle batteries and SCs 105 and verified the effectiveness and reliability of hybrid power through 106 Matlab/Simulink simulations and experiments. Gong et al. [63-66] established a 107 108 composite energy storage system composed of HSCs and batteries for simulation and experimental research, which improved the voltage drop of battery and greatly 109 improved the starting performance. 110

Having said all of the above, the existing hybrid energy storage system for 111 112 vehicle startup is mainly composed of SCs combined with VRLA batteries as well as lithium batteries in series and parallel mode. As a result, these give full play to the 113 114 high-power rate of SCs and high energy of batteries, which is faster and more fuel-115 efficient than a single energy storage system [67,68]. However, few scholars have 116 conducted comparative and experimental studies on the starting performance of HSCs and batteries, especially the comparative analysis of starting fuel consumption and 117 starting exhaust gas [69,70]. Hence, the design of an energy storage system with 118 battery and SC performance by HSC is of urgent need. 119

120 Based on the combination of supercapacitor and battery energy storage system, 121 this paper proposed an energy storage system module built at the cell level of HSCs, 122 of which the starting performance, fuel consumption, and exhaust emission effects of the vehicle were examined. First, two HSC energy storage systems were designed; 123 124 their electrochemical properties were tested. Second, the HSCs based on engine test 125 benches were compared with the start of the battery test. Third, the start fuel consumption and exhaust gas of HSCs and batteries were compared. The 126 127 experimental results showed that the HSC energy storage system had a significantly 128 shorter startup time and resulted in less frustration than other types of battery modules. Additionally, the performance in terms of fuel saving and emission reduction was 129 remarkable, and the fuel economy was improved. In the future, with the rapid 130 131 development of automobile industry and transportation industry, people have put forward higher requirements for automobile energy conservation, emission reduction 132 133 and safety performance. The development of an HSC energy storage system with high 134 efficiency that saves energy and is environmentally friendly is expected to replace the 135 traditional VRLA and LFP battery energy storage systems; this will be conducive to 136 improving the quality of vehicle starting performance. Moreover, the low long-term 137 cost of the HSC energy storage system has played an important role in accelerating its promotion and application and advancing its industrial development. As such, the 138

promotion of its industrial development has important significance and applicationvalue.

141 **2.** Experimental design

142 2.1. Selection of HSC monomers

143 Before the design of the energy storage system, the 18650 type 3.6 V/2200 F HSCs from Dongguan Gonghe Electronics Co., Ltd. was selected based on the voltage, 144 145 capacity, safety, and cost of the starting power supply. Its internal structure included 146 an electrode sheet, isolation film, pole, and shell. In addition, the coating on the 147 electrode sheet included an active material, conductive agent, and adhesive [71-74]. The active material was a mixture of various materials, including carbon material, 148 149 conductive polymer, and graphite-type carbon nitride. The carbon material had a core-150 shell structure [75,76], and its nuclear layer included graphene fiber and carbon 151 nanotubes. Its shell was composed of a functional layer of manganese dioxide [77-79]. The conducting polymer was a mixture of polyaniline, polythiophene, and polypyrrole 152 153 [80-84]. Composites of carbon materials and conductive polymers combine the best of 154 both types of materials and exhibit synergistic effects. The conductive polymer 155 provides the HSC, and the carbon material acts as the skeleton in the complex, supporting the conductive polymer to maintain its stability during the charging and 156 discharging cycle. [85-89]. The technical parameters (e.g., monomer) are presented in 157 158 Table 1. The Service life test data in the table were conducted by China CEPREI 159 Laboratory under the following experimental conditions (ambient temperature: 20°C±5°C, relative humidity: 25%-85%, ambient pressure: 86-106 kPa). The 160 161 corresponding test steps are as follows:

Step 1: Choosing 3 samples, using a constant voltage charging method, charge
with 0.5 A constant current to the rated voltage 3.6 V, until the current drops to 50
mA.

165 Step 2: The charged samples stored in an ambient for 5 minutes.

166 Step 3: Discharge at 0.5 A current to 2 V cut-off voltage.

167 Step 4: The discharged samples stored in an ambient for 5 minutes.

168 Step 5: Charge with 0.5 A constant current to the rated voltage 3.6V, until the 169 current drops to 50 mA.

170 Step 6: Step 2 to 5 repeated at least 300 times (one time defined as one cycle).

After testing according to the above steps, the total cycle number, N, iscalculated using the following (1):

173
$$N = \frac{C_0}{C_0 - C_n} \times n \times \left(\frac{1}{10}\right)^2 \times 80\%$$
 (1)

174 Where, C_0 is the initial discharge capacity, Ah; C_n is the remaining discharge capacity 175 after cycle test, Ah; n is the completed cycle number, times; I is the constant 176 discharge current in the cycle test, I = 0.5 A.

The calculation results show that the 3.6 V/2200 F HSC cells have no less than
80% capacity after more than 20000 cycles.

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- 180

Table 1 Technical specifications parameters of the HSC monomer.

Descriptions	Specification	Conditions
Nominal voltage (V)	3.6	
Nominal capacity (F)	2200	Standard discharge current
Capacity tolerance	±20%	Standard discharge current
Maximal recharging voltage (V)	3.65	
Maximal charging current (mA)	2000	
Discharge cut-off voltage (V)	2	
Maximal discharging current (mA)	6000	Pulse current discharge 30 A
Using temperature scope (°C)	-30-70	
Storage environment temperature	-20-65	
Storage environment humidity	\leq 85%	
Weight (g)	40	
Internal impedance (m Ω)	≤ 28	Upon fully charge (1 kHz)
Service life (times)	≥ 20000	Not less than 80% capacity
Size (mm)	65×Ф18	
Protection class	IP 30	

181 2.2. Assembly of HSC energy storage system



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Fig. 1. Design flow chart of energy storage system of HSCs: (a) selection of the
monomer; (b) 4S 16PModule; (c) fixed bracket; (d) confluence plat; (e) solder
the confluence plate; (f) stick insulated; (g) stick with shockproof foam; (h) 4
module packing; (i) access components and (j) energy storage system.

187 The independent design hybrid super capacitor starting power assembly process is shown in Fig. 1. First, the selection of voltage difference value was less than 30 mV, 188 189 such that poor internal resistance value was less than 0.1 m Ω in the monomer. In 190 addition, the 4S 16P monomer had a fixed bracket, spot welder welding junction 191 formation module, an insulated module, and a welding wire. Second, stick was 192 composed of shockproof foam. Finally, the four modules were packed and connected to the BMS, diodes, weak current switches, and other accessories, thereby generating 193 194 the HSC module energy storage system. The system was designed with a rated 195 voltage of 12 V and a rated capacity of 70 Ah. Furthermore, a 12 V/50 Ah HSC 196 module was composed of four 4S 12P modules and was designed in the same way. Its 197 technical specifications are shown in Table 2. The technical parameters of the 198 purchased LFP battery and Camel VRLA battery from Guangzhou Geyu Electronics 199 Co., Ltd. are shown in Table 3.

Specifications	12 V/50 Ah HSCs	12 V/70 Ah HSCs
Serial mode	4S 48P	4S 64P
Storage capacity (Ah)	50	70
Rated voltage (V)	12	12
Maximum charging voltage (V)	14.4	14.4
Internal resistance (m Ω)	22.31	20.12
Product weight (kg)	11.24	13.8
Operating temperature (°C)	-30-70	-30-70
Service life (times)	\geq 20000 (Not less than 80% capacity)	\geq 20000 (Not less than 80% capacity)
Product size (mm)	255×165×215	325×165×215
Protection class	IP 30	IP 30

203 Table 2 Technical specifications parameters of the energy storage system independent designs.

 Table 3 Technical specification parameters of the purchasing energy storage systems.

Specifications	12 V/70 Ah LFP batteries	12 V/70 Ah VRLA batteries	
Serial mode	4S 3P	6S 1P	
Storage capacity (Ah)	70	70	
Nominal voltage (V)	12	12	
Maximum charging voltage (V)	14.6	16	
Self-discharge	5%	10%	
Product weight (kg)	8	14.78	
Operating temperature (°C)	-20-55	-10-60	
Product size (mm)	278×175×190	250×160×200	
Protection class	IP 30	IP 30	

206 2.3. Constructing experimental test platform

207 2.3.1. Fundamental electrochemical performance test platform



208 209 Fig. 2. Test platform for the electrochemical performance of HSC energy storage systems. The electrochemical performance test platform of the energy storage systems of 210 211 HSCs are presented in Fig. 2. This platform was mainly composed of a special battery charge/discharge aging machine and a data analysis system. Its technical parameters 212 are shown in Table 4. It was used to test the charge/discharge voltage and capacity 213 variation characteristics of the energy storage systems of HSCs. The crocodile clip of 214 215 the test line of the battery charging/discharging aging special machine was connected 216 to the positive and negative poles of the starting power of the HSCs to conduct the charging/discharging test of the starting power of the HSCs. In addition, the data 217 218 analysis system was connected to the battery charge/discharge aging special machine 219 for experimental data transmission, storage, and analysis.

 Table 4 Technical specifications parameters of electrochemical test platform.

Laboratory equipment		specification
Battery charging/dischargin aging machine	ng special	Voltage range: 0–100 V
		Charging current: 0–10 A
		Discharge current: 0–20 A
		Charge constant voltage cut-off current: < 10 mA
		Charging mode: Constant current and constant voltage charging Discharge patterns: Constant exile electric
		Charging cut-off condition: Voltage, current, relative time, overcharge protection
		Discharge cut-off conditions: voltage, relative time, over-discharge protection
	Laboratory equipment Battery charging/dischargir aging machine	Laboratory equipment Battery charging/discharging special aging machine

Cycle range: 1–999 times Precision: ± 1 ‰

221 2.3.2. Startup performance test platform

Fig. 3 presents the experimental platform for testing the startup performance of 222 HSCs and batteries. The experimental platform included: the technical parameters of 223 the engine test bench, 12 V/50 Ah HSCs module, 12 V/70 Ah HSCs module, 12 V/70 224 225 Ah LFP batteries module, 12 V/70 Ah VRLA batteries module, BMS, communication 226 box, PC host computer, and noise tester (Table 5). Among them, the 2017 Magiten B8 227 engine test bench (Guangzhou Wangzhong Education and Technology Co., Ltd.) was 228 included. The 12 V/70 Ah HSCs module was installed on the test bench, and BMS 229 was connected to collect the voltage, current, temperature, and SOC estimation. The 230 data was transmitted to the PC upper computer by connecting the UART communication box, and the PC upper computer received the data and stored it. 231 232 Additionally, the noise was tested by the noise tester. The same scheme was used to 233 replace the 12 V/70 Ah HSC module with the 12 V/50 Ah HSC module, the 12 V/70 234 Ah LFP battery module, and the 12 V/70 Ah VRLA battery module for experiments. All experiments were carried out on the same experimental bench. Finally, the data of 235 the test platform in this experiment was compared, from which the peak starting 236 current, voltage drop, and instantaneous power change of the four energy storage 237 systems were analyzed. The starting effect was then studied, and the startup capability 238 239 was analyzed by a comparison with the startup noise.



240 241

Fig. 3. HSCs and batteries startup performance test platform.

242 Table 5 Technical specifications parameters of startup performance experimental equipment.

Laboratory equip	ment	Specification				
Engine test bench	1	Specifications and models: 2017 B8 Volkswagen Magotan 2.0T- EA888				
		Maximum horsepower: 220 Ps				
		Maximum torque: 350 Nm				
		Transmission: 7-speed wet dual clutch				
BMS		Model and specification: JBD-SP04S034				
		Cell specification: 3-4 string				
		Port type: Charge and discharge with the same port				
		Single voltage: 2.2–3.75 V				
		Continuous discharge current: \leq 250 A				
		Power consumption: $\leq 25 \text{ mA}$				
		Internal resistance of the protection plate: $\leq 10 \text{ m}\Omega$				
		Operating temperature: -30°C-70°C				
Communication box		UART communication				
Noise measuring instrument		Model and specification: SL-1350 B				
		Measurement range: Lo= $35-100 \text{ dB}/\text{Hi} = 65-130 \text{ dB}$				



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Fig. 4. HSCs and batteries startup fuel consumption test platform.

246 Fig. 4 presents the experimental test platform for starting fuel consumption. The test instruments and equipment of this experimental test platform included: 2017 247 248 Magiten B8 engine test bench, 12 V/50 Ah HSCs module, 12 V / 70 Ah HSCs module, 12 V/70 Ah LFP batteries module, 12 V/70 Ah VRLA batteries module, small oil 249 250 consumption flowmeter, and paperless recorder developed by Axia Instrument Firm. This was placed in high-tech development zone. The device specifications are 251 252 summarized in Table 6. The original engine was improved, and a small fuel 253 consumption flowmeter was connected to the oil inlet pipe to collect the starting fuel 254 consumption flow rate and cumulative fuel consumption. The collected data were output through a paperless recorder. This experimental test platform was used to study 255 256 the starting time, fuel consumption flow rate, and cumulative fuel consumption of 257 four different energy storage systems each time. Further analysis on the fuel 258 consumption of the energy storage systems of the HSCs was performed every time.

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 Table 6 Technical specifications parameters of fuel consumption test equipment.

Laboratory equipment	specification
Micro-meter for fuel consumption	Type: GICAR
	Specification: 0.7 mm, 1.5–42 (L/h)
	Instrument coefficient: 0.3 (cm ³ /imp), 3333 (I/L)
	Temperature range: -10-100°C
	Level of accuracy: $\pm 2\%$
	Accuracy of repetition: $\pm 0.2\%$

	Overall size: 40×55×40 mm		
	Power supply: 4.5–24 VDC		
	Output: Open collector circuit		
Paperless recorder	Specifications and models:		
	R6200-A06-R02-PA1-SU-MD-VAC		
	Input: 220 VAC/50 Hz		
	interface: USB1.1/2.0 U disk		
	Precision grade: 0.5%		
	Output signal: Pulse output, 4-20 mA output, RS485 output		
	Medium temperature: -20-100°C		
	Protection grade: IP 65 (Waterproof level)		

260 2.3.4. Exhaust test platform

The exhaust gas experimental test platform was built according to the connection 261 262 mode in Fig. 5. The test instruments and equipment of the platform included: 263 technical specifications of 2017 Magton B8 engine test bench, 12 V/50 Ah HSCs module, 12 V/70 Ah HSCs module, 12 V/70 Ah LFP batteries module, 12 V/70 Ah 264 VRLA batteries module, NHA-506 tail gas analyzer, and standard tail gas (Table 7). 265 Among them, the tail gas analyzer was used to analyze the volume concentrations of 266 267 HC, CO, and CO₂ in the starting process of four different energy storage systems, and 268 the standard tail gas was used to calibrate the tail gas analyzer before starting. Through the experimental platform, the volume concentrations of HC, CO, and CO₂ 269 270 in the startup exhaust gas of each energy storage systems were compared and studied. The exhaust emission performance of the energy storage systems of the HSCs was 271 272 analyzed.



Fig. 5. HSCs and batteries startup exhaust test platform.

 Table 7 Technical specifications parameters of exhaust test equipment.

Laboratory equipment		Specifications
Exhaust analyzer	gas	Specification: NHA-506 Including instrument host, short catheter, prefilter, sampling tube, sampling probe, and embedded micro printer Implementation standard: "Q/NH4 Vehicle Emission Gas tester"
		Key components: Nitrogen and oxygen sensor, oxygen sensor, main control board, and optical platform Test principle: The principle of infrared absorption method
		The environment temperature: + 5°C-+ 40°C
		Relative humidity: 5%-95% (The condensation)
		Atmospheric pressure: 70 kPa-106 kPa
		HC (hexane equivalent) measurement range: $(0-10000) \ge 10^{-6}$ vol
		CO measurement range: $(0-10) \times 10^{-2} \text{ vol}$
		CO_2 measurement range: (0–18) x10 ⁻² vol
		The relative error: $\pm 5\%$
		Warm up time: 10 minutes
		Output interface: RS-232C
		Overall dimensions (length \times width \times height): 450 \times 260 \times 180 mm
		Weight: 7 kg
Standard	for	Gas standard number: GBW (E) 080449
exhaust gas		C_3H_8 Component concentration: 0.314×10^{-2}
		CO Component concentration: 3.55×10^{-2}
		CO_2 Component concentration: 7.9×10^{-2}

276 2.4. Experimental test

277 2.4.1. Electrochemical performance testing

The electrochemical performance test experiment of the self-designed HSC 278 energy storage systems was carried out at room temperature (25.6°C). First, the 12 279 280 V/50 Ah and 12 V/70 Ah HSC energy storage systems were divided into two groups. Second, the charging test of the energy storage system was performed. Before the test, 281 282 the HSCs were discharged with a current of 20 A to a cut-off voltage of 9 V, and let 283 stand for 30 min. They were then charged to 14.4 V with a current of 10 A. Finally, 284 the discharge test of energy storage system was carried out. Before the test, the HSCs were charged with a current of 10 A to a rated voltage of 14.4 V, let stand for 30 min, 285 and then discharged with a current of 20 A to a cut-off voltage of 9 V. Each group was 286 287 tested 6 times, and the average value of the data was analyzed to draw the curve of 288 voltage, capacity, and time. Moreover, the 12 V/70 Ah hybrid supercapacitor energy storage system module has been completed two charge-discharge cycle tests with 10A 289 290 current. And Coulombic efficiency (η) of HSCs are calculated through the following Eq. (2) [90,91]: 291

$$\eta = \frac{c_d}{c_s} \times 100\% \tag{2}$$

293 Where, C_d is the discharge capacity and C_c is the charging capacity.

294 2.4.2. Startup performance testing

The startup performance test was carried out at room temperature (26.2°C). The 295 296 experimental object was 2017 Magotan B8 test bench, and the experiment was carried 297 out according to the National Standard GB/T 18297-2001 "Automobile Engine 298 Performance Test Method". First, the HSC module of 12 V/50 Ah and 12 V/70 Ah, the 299 VRLA battery module of 12 V/70 Ah, and LFP battery module of 12 V/70 Ah were fully charged and allowed to stand for 30 min. During this period, the engine with the 300 301 backup power supply was started and run at idle speed for a period of time to increase the temperature to normal working state. The engine was then shut down. The full of 302

303 the start of the electric power were then conducted on the engine test bench to start the 304 experiment. Four kinds of energy storage systems were divided into four groups for the experiment. Each group carried out 12 experiments, each including idle time 305 306 launched for a total of 1 min. Before each start experiment, the energy storage system 307 was fully charged to the rated voltage and let stand for 30 min. The average value was 308 taken to draw the voltage and current curves. Furthermore, a noise tester was used to 309 test the startup noise during the starting process. The ambient noise was 50.28 dB. The noise tester for each test was placed in the same position, and the data was 310 recorded to draw a startup noise curve. 311

312 *2.4.3. Startup fuel consumption testing*

Startup fuel consumption experiment was conducted at room temperature (26.3°C) 313 and followed the unified detection standard GB/T19233-2008 "Light Vehicle Fuel 314 315 Consumption Test Method". The volume method was used to measure fuel 316 consumption. As compared to the mass method, the operation of weighing fuel 317 consumption was simpler, and the result was more accurate. According to the above 318 starting performance test, the engine was preheated and the starting power was fully 319 charged and let stand for 30 min. The four energy storage systems were divided into 320 four groups for the experiment, wherein each group was started 25 times. Before each 321 startup, the energy storage system was fully charged to the rated voltage and let stand 322 for 30 min. The data were exported through the paperless recorder to analyze the fuel 323 consumption flow rate and cumulative fuel consumption at each startup.

324 2.4.4. Startup exhaust testing

The startup exhaust test will be carried out at room temperature (26.2°C). The test was carried out according to the working principle and installation requirements of NHA-506 exhaust analyzer, and according to the national "Emission Limits and Measurement Methods of Exhaust Pollutants for Ignition Engine Vehicles with Double Idle Speed Method and Simple Working Condition Method". Before the test, the engine was allowed to heat. During the test, the tail gas analyzer was first 331 preheated for 500 s. The air tightness and sensor aging were then checked, after which 332 the standard gas calibration and zero calibration were performed. Finally, the 333 sampling probe was inserted into the exhaust pipe and fixed. The four energy storage 334 systems were divided into four groups for the experiment. Each group was started 12 335 times, and the engine was started and stopped at idle speed for 1 min each time. The 336 data of the starting process was recorded and the volume concentration changes of HC, 337 CO, and CO₂ were analyzed when starting from different energy storage systems.

338 **3. Results and discussion**



339 *3.1. Electrochemical performance analysis*

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Fig. 6. Charge/discharge curves of HSCs: (a) voltage, and (b) capacity.

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According to the above design requirements, one set of 12 V/70 Ah and one set 344 345 of 12 V/50 Ah HSCs were assembled. In addition, the charge/discharge tests were completed. According to Fig. 6a, the voltage trends of charge/discharge of the two 346 HSCs were consistent. In the charging stage, 10 A constant-current charging was 347 adopted, and the voltage first jumped from 11.18 V to 12.48 V and then slowly 348 349 increased to 14.4 V. This was due to the rapid charging characteristics of the HSC, which had a voltage jump change. In the discharge stage, 20 A constant current was 350 351 used, and the voltage rapidly dropped from 13.10 V to 12.35 V, then slowly dropped,

352 and finally exhibited a sharp drop to 9 V. These observations were due to the rapid voltage drop at the beginning of discharge, which is characteristic of HSCs. With the 353 delay of the discharge time, the capacity decreased, thereby resulting in a sharp 354 355 voltage drop. The analysis of the results in Fig. 6b show that the charging capacity of the 12 V/50 Ah HSCs was 53 Ah and the discharge capacity was 40 Ah. The charging 356 357 capacity of the 12 V/70 Ah HSCs was 68 Ah, and the discharging capacity was 50 Ah. 358 The discharging capacity was affected by the cut-off voltage of 9 V. Hence, the 359 discharging capacity was smaller than the charging capacity. The actual capacity of 360 the energy storage systems met the design requirements. Moreover, the 12 V/70 Ah 361 HSCs energy storage system designed by us carried out two charge-discharge cycles 362 at a current of 10 A, with each cycle of about 15 h. The average charged capacity is 68.625 Ah, the average discharged capacity is 68.108 Ah, and the Coulomb efficiency 363 is 99.25%. It shows that charge storage rather than parasitic reaction is dominant. 364

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366 *3.2. Startup performance Analysis*

To illustrate the startup advantages of the HSC energy storage systems, the energy storage systems of LFP batteries module and LFP batteries module were compared. In addition, changes in the starting voltage, current, instantaneous power, and startup noise were analyzed.

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Fig. 7. Multiple starts curves of four energy storage systems: (a) average current; (b) average
voltage; (c) average instantaneous power and (d) average noise.

376 The average current curves of the four power supplies during multiple starts are 377 shown in Fig. 7a. The peak value appeared during the starting process. At this time, 378 the engine starting motor drove the crankshaft to rotate. A large resistance moment 379 and a low starting motor speed were observed, resulting in high current. The current 380 on the right side of the peak current dropped slowly, indicating that the speed of the 381 starting motor rose and the resistance decreased. The average current released by 12 382 V/70 Ah HSCs reached 240 A, which was larger than the average current released by 12 V/70 Ah LFP batteries module and VRLA batteries module of 200 A. The average 383 release current of 12 V/50 Ah HSC was smaller than that of 12 V/70 Ah HSC. When 384 the energy storage systems was finished, the generator charged the energy storage 385 386 systems, thereby generating a negative current and producing slow and stable changes 387 in the charging current of the HSC.

The average voltage curves of the four energy storage systems during multiple 388 389 startups are elaborated in Fig. 7b. The voltage dropped rapidly during startup. The starting voltage of 12 V/70 Ah LFP batteries module dropped from 13.5 V to 12.3 V, 390 391 and the average voltage declined to 1.2 V. The starting voltage of 12 V/70 Ah HSCs decreased from 13.2 V to 11.2 V, with an average voltage drop of 2 V, followed by 12 392 393 V/50 Ah HSCs. The VRLA batteries module startup voltage dropped from 13.4 V to 394 9.9 V, with an average voltage drop of 3.5 V reaching the maximum. In the charging stage, the voltage of 12 V/50 Ah and 12 V/70 Ah HSCs quickly rose and appeared 395 396 higher than the initial voltage. In comparison, the voltage of 12 V/70 Ah LFP batteries 397 module rose slowly, and the voltage of VRLA batteries module showed obvious 398 fluctuations.

According to the analysis of the average instantaneous power of the four energy 399 storage systems during multiple starting (Fig. 7c), the instantaneous power rose 400 401 sharply at the beginning of startup. The 12 V/70 Ah HSC had a maximum average 402 instantaneous power of 2700 W. In comparison, the average instantaneous power of 403 50 Ah HSC was small. However, it was relatively close to the average instantaneous 404 power of 12 V/70 Ah LFP battery. The 12 V/70 Ah VRLA battery had a minimum 405 average instantaneous power of 2000 W, and the average instantaneous power of the 406 four energy storage systems gradually decreased. In addition, negative power was 407 observed after startup indicating the start of charging.

According to the noise test of four energy storage systems in multiple starts (Fig. 7d), the maximum noise in the starting process of 12 V/70 Ah HSC was about 5 dB higher than that of 12 V/70 Ah VRLA battery module. In comparison, the average noise of the 12 V/70 Ah LFP battery module was close to that of the 12 V/50 Ah HSC. In addition, the average starting noise was less than that of the 12 V/70 Ah HSC. Under the condition that the rated torque was not exceeded, the 12 V/70 Ah HSC released a large current and showed a small voltage drop after starting, which then

- 415 increased the instantaneous startup power and started engine torque augmentation. As
- 416 such, the speed quickened, resulting in greater noise.





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419 Fig. 8. Multiple starts curves of four energy storage systems: (a) startup time;, and (b) average fuel
420 consumption flow rate.

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Fig. 8a presents the time curves of the four energy storage systems during several
startups. The starting time of the 12 V/70 Ah HSC was significantly shorter than that
of the 12 V/70 Ah VRLA battery module. In addition, the starting time of the 12 V/50
Ah HSC and 12 V/70 Ah LFP battery module were slightly shorter than that of the 12
V/70 Ah VRLA battery module.

Fig. 8b shows the average fuel consumption flow rate curves of the four energy storage systems following several startups. The engine had an average fuel consumption flow rate of 72 mL/min in idle state and showed stable operation. In addition, the HSC exhibited a shorter average fuel consumption velocity fluctuation time.





Fig. 9. Fuel consumption curves for multiple starts of four energy storage systems.

The starting fuel consumption curves of the four energy storage systems after 434 several startups (Fig. 9) showed an average starting fuel consumption distribution for 435 12 V/70 Ah HSC of <2.9 mL. In comparison, the average starting fuel consumption 436 437 distribution of the 12 V/70 Ah VRLA battery module was above 3.1 mL, indicating a 438 change in the fuel saving effect of the 12 V/70 Ah HSC. Furthermore, the average starting fuel consumption of the 12 V/50 Ah HSC and 12 V/70 Ah LFP battery 439 440 module was between 2.9 mL and 3 mL. In addition, its fuel saving effect was between 12 V/70 Ah HSC and 12 V/70 Ah VRLA battery module. The 12 V/70 Ah VRLA 441 442 battery module had an eighth start fuel consumption of 3.25 mL or more possibly due 443 to slow VRLA battery module voltage recovery. As a result, exceedingly low voltage and a small current were produced, thus increasing the startup time. 444



Table 8 Comparison and analysis of four energy storage systems in multiple starts modes.

Data	12 V/70 Ah HSCs	12 V/50 Ah HSCs	12 V/70 Ah LFP batteries	12 V/70 Ah VRLA batteries
Mean startup time (s)	1.567	1.658	1.669	1.926
Average startup fuel consumption (mL)	2.864	2.912	2.958	3.107

Idle fuel consumption flow	72	72	72	72
rate (mL/min)				

As demonstrated in Table 8, the average starting time and average starting fuel consumption of the four energy storage systems are different to a certain extent. As compared to the 7.82% fuel saving of the VRLA battery module, the 12 V/70 Ah HSC had the most obvious fuel-saving effect. As compared with LFP battery module, the fuel saving effect was reduced by 3.18%. In comparison with the 12 V/50 Ah HSC, the fuel saving effect was weak (1.65%).



452 *3.4. Startup exhaust analysis*

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Fig. 10. The tail gas curves of four energy storage systems in multiple startup: (a) HC volume
concentration; (b) CO volume concentration, and (c) CO₂ volume concentration.

457 The tail gas of the four energy storage systems in multiple startup experiments 458 were analyzed (Fig. 10a). The volume concentration of HC was the lowest in the 459 starting process of 12 V/70 Ah HSC. The volume concentration of HC in the starting 460 process of 12 V/50 Ah HSC was close but slightly higher to that of the 12 V/70 Ah LFP battery module. In addition, the maximum HC volume concentration of the 12 461 V/70 Ah VRLA battery module reached 420×10^{-6} vol during startup. However, the 462 HC volume concentration first rose sharply and then exhibited a slow decline due to 463 464 engine starting. As such, the burning temperature was lower and the residual gas in cylinder quantity was large, thereby creating a relatively rich mixture and causing 465 insufficient combustion and larger HC emission concentration. At a stable operation, 466 flow mixing in the cylinder was disturbed, such that increased eddy diffusion 467 promoted burning and reduced the HC emission concentration. The low volume 468 469 concentration of HC when the 12 V/70 Ah HSC started was due to the larger instantaneous power, shorter startup time, and faster starting. This allowed faster 470 starting to reach a stable speed to promote combustion and lower the volume 471 472 concentration of HC.

Fig. 10b presents the starting process, where the volume concentration of CO rose 473 sharply at first, decreased slowly, and gradually stabilized. The start engine speed was 474 475 lower, the volume was limited, thereby creating a rich mixture that affected the 476 concentration of CO generated by the mixture concentration. However, not enough 477 oxygen was allowed for the fuel carbon combustion into CO₂, thus generating a large amount of CO. Afterwards, the engine speed increased to a stable operation, thereby 478 479 increasing the volume and expanding the oxygen content to promote carbon transformation into CO₂. This ultimately resulted in a decrease in the CO content. The 480 481 CO volume concentration was the lowest when the 12 V/70 Ah HSC first started, and 482 the CO volume concentration was higher when the 12 V/50 Ah HSC and the 12 V/70 483 Ah LFP battery module started. However, the volume concentration of HC was the 484 highest when 70 Ah VRLA battery module started. In addition, the time to reach the 485 maximum value had a certain delay. The 12 V/70 Ah HSC released a larger current 486 and smaller voltage drop when starting, which resulted in a larger instantaneous 487 starting power and a rapid increase in the starting speed. As a result, the air intake and 488 the content of oxygen increased, thereby producing fuller carbon combustion and 489 enhanced conversion into CO₂. These resulted in a lower CO and better emission 490 reduction effects during the startup process.

491 According to Fig. 10c, on the whole, the volume concentration of CO_2 rose 492 sharply at first and then slowly increased. The volume concentration of CO₂ 493 continuously increase with the rapid increase of engine speed at the beginning of startup. As the engine gradually stabilized, the volume concentration of CO₂ rose 494 slowly and stabilized at a certain value. The CO₂ volume concentration was 495 496 significantly higher when the 12 V/70 Ah HSC was started. In addition, the CO₂ 497 volume concentration was lower when 12 V/50 Ah HSC and 12 V/70 Ah LFP battery 498 module were started. In comparison, the CO_2 volume concentration was the lowest when 12 V/70 Ah VRLA battery module was started. This was mostly predominant 499 when the 12 V/70 Ah HSCs were started, which resulted in a fuller HC combustion, 500 higher carbon combustion, and more CO₂, ultimately increasing the volumetric 501 concentration of CO₂. 502

503 4. Conclusions and future recommendations

504 *4.1. Conclusions*

Based on the HSC, a set of 12 V / 50 Ah and 12 V/70 Ah energy storage systems were designed in this paper, which were assembled and tested. Through the starting performance, energy-saving and emission-reduction experiments, the 12 V/70 Ah VRLA battery module and 12 V/70 Ah LFP battery module were compared, from which the following conclusions were drawn:

(1) An electrochemical performance test was performed on the self-designed 510 The results indicated 511 HSC energy storage system. that the 512 charging/discharging characteristics of 12 V/50 Ah and 12 V/70 Ah HSC were consistent. The charging/discharging voltage first jumped up or down 513 514 and then slowly changed to the cut-off voltage, which reflects the high 515 energy characteristics of the combination of the SC and battery. In addition, 516 the actual capacity of the energy storage system met the design requirements. (2) As compared to the starting of 12 V/70 Ah VRLA battery module and 12 517 518 V/70 Ah LFP battery module, the starting instant release current of the 12 V/70 Ah HSC was larger, the voltage drop was smaller, and the starting 519 520 instantaneous power was larger. These were beneficial for rapid starting and reducing the sense of frustration. However, as the starting torque increased, 521 522 the resulting starting noise also increased. In addition, the 12 V/50 Ah and 12 V/70 Ah HSCs started to release currents at a similar speed. The voltage 523 524 rose significantly and the current consistently changed during the charging 525 phase, which was conducive to absorbing current.

- (3) From the fuel consumption experimental data, the starting time of the 12
 V/70 Ah HSC was short, and the fuel consumption during stable operation
 was 72 mL/min. As compared to the 12 V/70 Ah VRLA battery module, the
 fuel-saving effect was the most obvious. As compared to the 12 V/70 Ah
 LFP battery module, the fuel-saving effect decreased by 3.18%. Compared
 with the 12 V/50 Ah HSC, the fuel-saving effect was not obvious. On the
 whole, it showed good fuel economy.
- (4) Hence, through the analysis of experimental data, it can be concluded that
 the volume concentration of HC and CO in the tail gas was low and the
 concentration of CO₂ was high when the 12 V/70 Ah hybrid HSC started,
 indicating that the fuel combustion was more sufficient during startup and
 had obvious emission-reduction effects

538 4.2. Future recommendations

539 Based on the above review and analysis, the following future development 540 opportunities and challenges of HSC energy storage system are suggested:

541 (1) Considering the needs of high starting power and long-term continuous542 power, HSC combine the advantages of high-power density and high-energy

543 density. In addition, they have superior starting performance as an 544 automotive energy storage system. It is worth noting that improving the 545 energy density while keeping the power density as high as possible will be 546 one of the hot spots in future research.

- (2) As a kind of vehicle startup energy storage system, the problems of startup 547 548 time, startup frustration, and energy decay during frequent startup will directly affect the user's experience. Therefore, during the startup process, 549 future research should focus on the aging of energy storage systems and 550 performance degradation. Considering the actual operating conditions of the 551 552 vehicle (climbing, acceleration, starting, collision, low temperature), the 553 starting performance of the complex environment is worth further 554 exploration.
- (3) When a car starts to stumble, it will consume more fuel, and the main reason
 for the slump is the lack of power supply from the energy storage system.
 Therefore, a HSC energy storage system with high energy density and low
 self-discharge rate needed to reduce fuel consumption. In addition, HSC will
 be the most promising future energy storage system application solution in
 automotive energy recovery systems.
- (4) Reducing exhaust emissions is also a key factor to measure the starting
 performance of vehicles. The superior emission reduction performance of
 HSCs is more conducive to green environmental protection, but other
 components of exhaust also need to be further studied. In addition, the
 development of a high-performance, high-security, low-cost, and
 maintenance-free energy storage system is of urgent need.

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