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ORIGINAL PAPER

Defatted spent coffee grounds-supported cobalt catalyst as a promising supercapacitor electrode for hydrogen production and energy storage

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Abstract

The effect of several parameters, such as different Co^{2+} ratios, burning temperatures, and burning times, was examined by using defatted spent coffee grounds (DSCG) as organic waste to obtain the most effective catalyst for producing hydrogen. Under optimum conditions, the most active catalyst/metal ratio was obtained by burning 50% Co^{2+} at 400 °C for 90 min. To measure the time-dependent amounts of hydrogen, 0.1 g of DSCG-Co catalyst was dissolved in 10 mL of a methanol solution containing 0.25 g sodium borohydride ($NaBH_4$) at 30 °C. The maximum hydrogen generation rate obtained from the methanolysis of $NaBH_4$ at 30 and 60 °C was found to be 8749 and 17,283 mL min^{-1} $gcat^{-1}$, respectively, and the activation energy of the catalyst was found to be 23.2 kJ mol^{-1}. FTIR, ICP-OES, XRD, BET, and SEM–EDX analyses were performed for the characterization of the prepared DSCG-Co-Cat catalyst. Furthermore, a supercapacitor cell was constructed by using this catalyst as an active substance for electricity storage. The specific capacitance of the electrode at the current density of 1 A/g was calculated as 67 F/g for two-electrode systems. The results of electrochemical analysis of the prepared supercapacitor were found to be similar to the ideal supercapacitor curves. The obtained capacitance values are at very good levels in terms of the capacity and cost factors. The results indicated that the multifunctional capacitor-catalyst material produced by Co-doped waste coffee could constitute an important element in a hybrid system that includes capacitor and catalyst systems that can be installed in the future.

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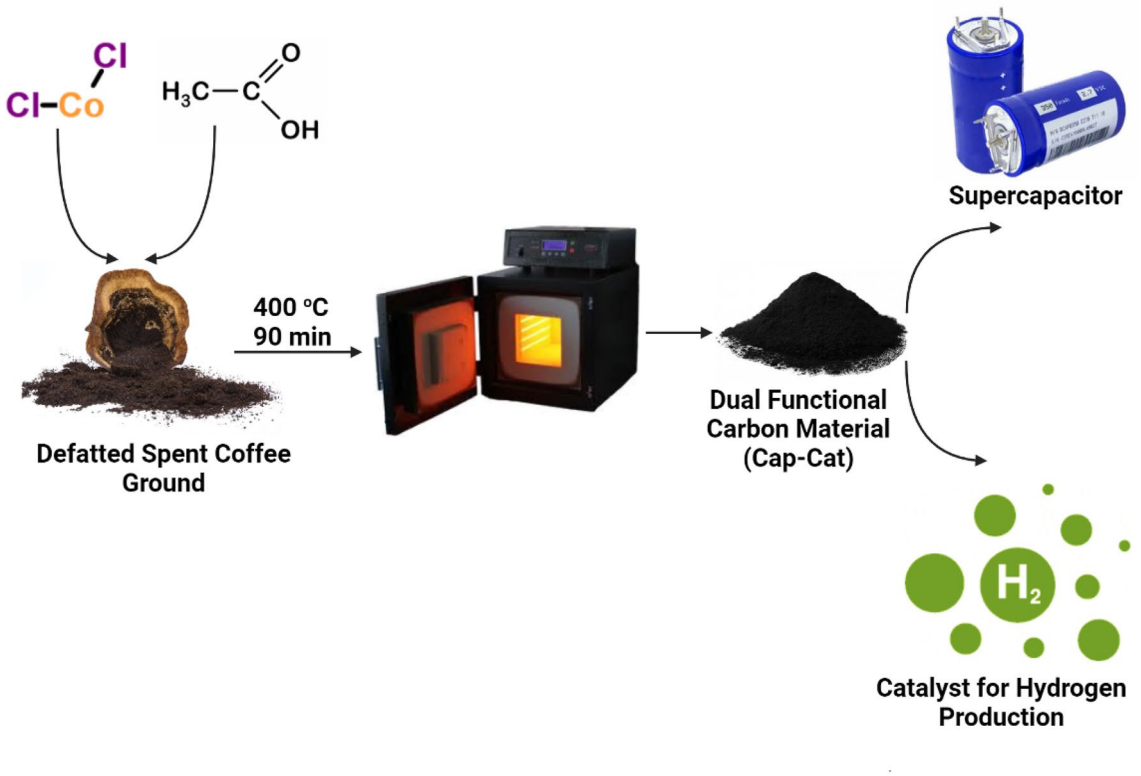
Graphic abstract



Keyword Defatted spent coffee grounds · Hydrogen · Catalyst · Capacitor-catalyst · Supercapacitor

Introduction

The demand for fossil fuels has been increasing due to the increasing world population. In line with this increase, several factors, such as carbon dioxide and methane emissions, which occur due to the consumption of fossil fuels, cause air pollution (Zahmakıran and Özkar 2006; Zerta et al. 2008; Liu et al. 2009). The amount of carbon dioxide (CO_2) in the atmosphere has increased to a threatening point. Therefore, the world needs new and clean energy that will meet the increasing need for energy, will not threaten nature, and is renewable and thus sustainable (Jean-Baptiste and Ducroux 2003). Greenhouse gases such as hydrogen, carbon dioxide, and methane are becoming attractive ways of meeting future fuel needs. In this case, the production of an environmentally friendly energy carrier, such as hydrogen, can play an important role in obtaining sustainable energy (Muradov and Veziroğlu 2008; Ibrahim 2014). It is known that hydrogen is not toxic and has high energy density and zero emissions and is therefore considered a clean fuel for fuel cells (Jacobson et al. 2005). However, before a hydrogen-based energy economy becomes feasible, many serious technical challenges need to be addressed.

One of the most challenging technical obstacles to the implementation of the hydrogen economy is stationary hydrogen storage. In-vehicle hydrogen storage systems must meet the strict requirements of gravimetric and volumetric energy densities because of their limited volume and permissible weight (Zhang et al. 2006). Because of its non-toxicity, safe storage and transport properties, and high hydrogen (H_2) content (10.8% by weight), $NaBH_4$ is considered a likely source of H2 for real applications. Hydrolysis and methanolysis of $NaBH_4$ require the use of catalysts (Ozay et al. 2011; Schlapbach and Züttel 2011). Hydrolysis is inconvenient because $NaBH_4$ reacts at low temperatures and has low conversion power and slow reaction kinetics. Methanolysis, however, has several advantages over hydrolysis. Methanol is widely used as a solvent and can be easily obtained from renewable sources such as plants, trees, and biomass or feedstock. However, methanolysis of $NaBH_4$ can exhibit rapid reaction kinetics, even at low temperatures (≤ 0 °C), and higher catalytic performance at low activation energy compared to

hydrolysis (Lo et al. 2007; Fernandes et al. 2010; Sahiner 2017). Equation (1) shows the methanolysis of $NaBH_4$.

$$NaBH_4+4CH_3OH \rightarrow NaB(OCH_3)_4+4H_2 \quad (1)$$

Generally, the methanolysis in Eq. (1) shows a higher hydrogen generation rate (HGR) at lower temperatures and shows better kinetic properties than the hydrolysis.

Energy production, especially from renewable energy sources, is highly dependent on external parameters. To use electrical energy more efficiently and meet the energy needs of consumers, energy must be stored. Among the various energy storage materials, supercapacitors have been preferred because they store and transfer energy more quickly than any other. While supercapacitors that store energy statically may store much more energy than capacitors, they can transfer this energy about ten times faster than electrochemical batteries (Pandolfo and Hollenkamp 2006). With the development of efficient electrode materials, high-performance supercapacitors can be designed (Sun et al. 2013). Materials to be used in making supercapacitor electrodes for high-capacity power applications must have a large surface area and high conductivity. Considering these parameters, carbon-based materials are among the most used materials in electrode production (Béguin et al. 2014). Biomass wastes in activated carbon groups are preferred because they have high carbon content and are cheap, abundant, and renewable (Jain et al. 2016; Tang et al. 2017). There are many studies on biomass-based supercapacitor electrodes, such as cherry stones, (Olivares-Marín et al. 2009), peanut shells (He et al. 2013), waste newspaper (Kalpana et al. 2009), and olive pits (Redondo et al. 2015). In our previous studies, we have shown that carbon materials called "cap-cats" (capacitor-catalysts) can be used multifunctionally as both catalyst material and supercapacitor material (Akdemir et al. 2021; Inal et al. 2021). Hence, together with catalyst studies, a supercapacitor was developed to determine the energy storage capacity of the material used.

In this study, a catalyst was prepared by using cheaper cobalt instead of precious metals such as Pt and Ru to obtain higher yields in the methanolysis of $NaBH_4$ using defatted spent coffee grounds (DSCG), which is one of the most abundant organic waste materials. This study is an environmentally friendly and sustainable inquiry into a way to produce value-added products from waste materials. The DSCG-Co catalyst (DSCG-Co-Cat) was synthesized by the treatment of a DSCG catalyst (Kaya 2020b) with 1 M CH_3COOH and $CoCl_2.6H_2O$ at different ratios, and DSCG-Co-Cat is relatively inexpensive compared to other catalysts prepared by precious metals. Various burning temperatures and burning times were used to test the optimization studies of DSCG-Co-Cat in $NaBH_4$ methanolysis experiments. Performance tests of the DSCG-Co-Cat catalysts were completed by the use of different $NaBH_4$ amounts, different catalyst amounts, different temperatures, and reusability tests. Finally, by the use of the DSCG-Co-Cat as an electrode active material, a supercapacitor cell with a two-electrode system was prepared. Electrochemical characterizations of electrodes were implemented by cyclic voltammetry (CV), electrochemical impedance spectrum (EIS), and galvanostatic charge discharge (GCD) curves.

Materials and methods

Preparation of DSCG-Co-Cat

The best acid concentration for DSCG used in the experiment was determined in our previous study, and this experiments used that acid concentration, 1 M CH_3COOH, (Kaya 2020b). For each experiment, 20 ml of 1 M CH_3COOH (99.5%) and $CoCI_2.6H_2O$ at different concentrations (10%, 20%, 30%, 40%, and 50%) were added to 5 g of the DSCG catalyst and stirred at 200 rpm for 10 min. Afterward, it was held in an oven at 80 °C for 24 h, followed by burning in a furnace at 400 °C for 90 min under the inert gas medium (N_2). The activity of the DSCG-Co-Cat catalysts containing various Co^{2+} concentrations was investigated by the use of a methanolysis of $NaBH_4$ (≥ 98%) to determine the optimum Co^{2+} ratio. To obtain optimum conditions, various burning temperatures (300, 400, 500, and 600 °C), various burning times (30, 45, 60, and 90 min), various concentrations of $NaBH_4$ (1%, 2.5%, 5%, and 7.5%), and various concentrations of DSCG-Co-Cat catalyst (0.05, 0.1, 0.15, and 0.25 g) were tried. Finally, the DSCG-Co-Cat was analyzed by several techniques, such as Fourier transform infrared (FTIR) spectra, scanning electron microscopy with energy-dispersive X-ray (SEM–EDX), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and inductively coupled plasma optical emission spectroscopy (ICP-OES). Activation energy was calculated using the Arrhenius equation, Eq. (2).

$$\ln(k) = \ln(A) - Ea/RT \quad (2)$$

In Eq. (2), k is the reaction rate constant, Ea is the activation energy, R is the gas constant (8.314 J K^{-1} mol^{-1}), and T is the absolute temperature. FTIR analyses of the DSCG and DSCG-Co-Cat samples were performed on a Nicolet IS10 spectrometer in the 4000 − 400 cm^{-1} at 4 cm^{-1} resolution. The crystal structure of the DSCG and DSCG-Co-Cat samples was investigated in the range of 4–80 °C by XRD (Bruker D8 Advance, CuKα radiation; λ = 0.15418 nm). The surface morphology of the DSCG and DSCG-Co-Cat samples was analyzed by SEM–EDX (Hitachi S-4300). BET calculation was used to determine the surface area. The Barrett–Joyner–Halenda (BJH) method was used to determine

the pore size distributions. The samples were degassed overnight in a vacuum. Finally, to determine trace elements in the DSGC and DSCG-Co-Cat samples, analyses were performed by ICP-OES (PerkinElmer Optima 2200 DV).

Preparation and electrochemical characterization of supercapacitor electrodes developed from DSCG-Co-Cat material

At this stage of the study, the best material obtained as a result of the catalyst experiments, the DSCG-Co-Cat catalyst, was selected, and a supercapacitor cell was designed using this material. The electrode mixture was prepared by using the catalyst material (80 wt %) as an active ingredient, a nanotube (10 wt %) as a conductivity-enhancing material, and polyvinylidene fluoride (PVDF; 10 wt %) as a binder. To dissolve the PVDF, N-methyl-2-pyrrolidone (NMP) was used. This mixture was kept in an ultrasonic mixer for 10 min, then it was mixed in a magnetic stirrer for 2 h, and a homogeneous substance was obtained. This mixture was then sprayed onto the current collector nickel foam. To extract NMP from the mix, the electrodes were left for 24 h in a vacuum at 80 °C. Two identical circular anode and cathode electrodes, a thin separator paper, and 6 M KOH as the electrolyte solution were placed in a sealed aluminum test apparatus to configure the two-electrode cell. Then, the electrochemical characterization of the supercapacitor was implemented at room temperature by the PalmSens4 Electrochemical Analyzer using galvanostatic charge–discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The electrode's gravimetric capacitance was computed based on Eq. (3)

$$C = 2I\Delta t/m\Delta V \tag{3}$$

by using the GCD curves, where ΔV is the potential difference during discharge, I is the constant discharge current, Δt is the time elapsed during discharge, and m signifies one electrode's active material mass.

Results and discussions

Functional group analysis (FTIR)

The FTIR spectra of the DSCG and DSCG-Co-Cat catalysts are shown in Fig. S1. A broad band was observed at about 3306 cm^{-1} for raw DSCG, which shows a high carbohydrate and protein content, while a weaker band was observed in this region for the DSCG-Co-Cat catalyst treated with 1 M CH_3COOH and burned at 400 °C, indicating that carbohydrates and proteins broke down owing to both acid treatment and burning of DSCG (Yang et al. 2016). For DSCG, there were aliphatic C – H stretching peaks between 3000 and 2800 cm^{-1} and C–H bending peaks at 1519 and 1375 cm^{-1}. CO stretching bands of the carboxylic groups were observed at 1650–1600 cm^{-1}, a result of the protein contents of the DSCG. The C–N stretching peak at 1029 cm^{-1} was present in the FTIR spectrum of the DSCG, while it was weaker in that of the DSCG-Co-Cat catalyst (Vardon et al. 2013).

ICP-OES analysis

Table 1 shows the percentage of elements contained in the raw DSCG as derived by ICP-OES. According to the results, DSCG consists of four main elements (Ca, K, Mg, and P). Also, as shown in Table 1, other trace elements were recorded. When the catalyst was prepared by adding Co^{2+} with a metal ratio of 50% to DSCG treated with 1 M CH_3COOH, 20.07% Co adhered to the structure.

SEM–EDX analysis

Figure 1 shows the SEM images of raw DSCG (a), DSCG-Co-Cat (b), raw DSCG SEM–EDX (c), and DSCG-Co-Cat SEM–EDX (d) catalysts. The DSCG in (a) had an uneven structure, while DSCG-Co-Cat catalyst prepared by burning and the addition of acid and Co^{2+} became more even and porous. The DSCG-Co-Cat was homogeneously distributed on the surface of cobalt metals, as can be seen in (b). The raw DSCG contained C (67.8%), O (38.8%), and Cl (0.4%), while the approximate ratios of C (50%) and O (14.6%) decreased in the supported catalyst (DSCG-Co-Cat), whose chemical composition contained 23% Co. As a result, it is thought that the cobalt in the catalyst sintered as a result of combustion, increasing the catalyst activity.

XRD analysis

The XRD patterns for the raw DSCG (a) and DSCG-Co-Cat (b) catalysts at 2θ = 4–80 °C are presented in Fig. S3. For the raw DSCG, two separate peaks were observed for the carbon and sugar structures at 2θ = 7° and 24 °C, respectively. These

Table 1 ICP-OES analysis for raw DSCG

Elements	Raw DSCG (%)	Elements	Raw DSCG (%)
Al	0.0031	Mg	0.1347
B	0.0003	Mn	0.0031
Ba	0.0004	Mo	0.0007
Ca	0.0868	Na	0.0591
Cu	0.0021	Zn	0.0009
Fe	0.004	P	0.1798
K	0.4812	Pb	0.0002
Li	0.0003	Sr	0.0005

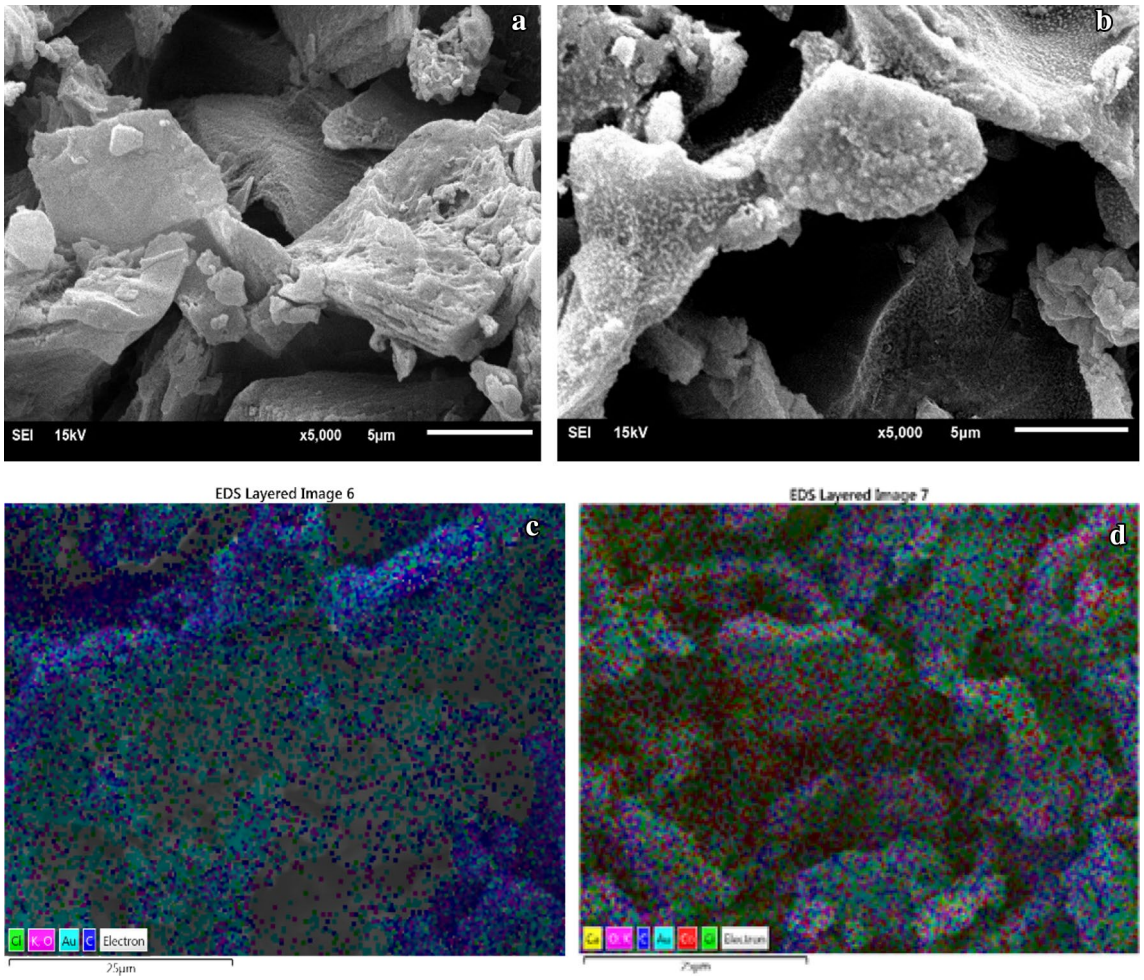


Fig. 1 Raw DSCG SEM (**a**), DSCG-Co-Cat SEM (**b**), raw DSCG SEM–EDX (**c**), DSCG-Co-Cat SEM–EDX (**d**)

typical peaks, which have a crystalline carbon and sugar structure, vanished for the DSCG-Co-Cat catalyst, as seen in Fig. S3b. Thus, it can be concluded that the structure of raw DSCG was significantly altered by the addition of the acid and Co, and the amorphous structure of raw DSCG was made crystalline by the addition of acid and after the burning processes (Perdana et al. 2018).

BET analysis

The BET surface area analysis was carried out for the raw DSCG and DSCG-Co-Cat catalysts prepared by the addition of 50% Co $^{2+}$ content and treated with 1 M CH_3COOH. A significant difference was found when the BET surface areas of the raw DSCG and the DSCG-Co-Cat were compared: the values were 23.474 m^2/g and 1.380 m^2/g, respectively. Thus, we can conclude that the surface of the raw DSCG was coated with cobalt and its surface area decreased. This result agrees with the SEM–EDX analysis.

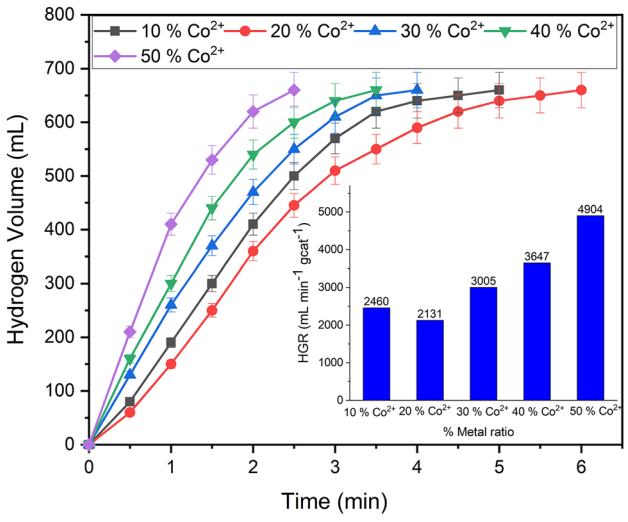


Fig. 2 The change of HGR of the media containing different Co $^{2+}$ concentrations as a function of time (reaction conditions: 2.5% $NaBH_4$, catalyst = 0.1 g, T = 30 °C, Vmethanol = 10 mL)

Effect of metal ratio

As shown in Fig. 2, the increasing concentrations of Co^{2+} added to the DSCG catalyst treated with 1 M CH_3COOH have a generally positive effect on the HGR. For the cobalt catalyst supported by the DSCG, the best result was the catalyst containing 50% cobalt. The reaction completion time for this catalyst was about 2.5 min, while the reaction completion time was 3.5, 4, 6, and 4.5 min for the catalysts containing 40%, 30%, 20%, and 10% Co^{2+}, respectively, due to the effect of reduced metal ratios.

After the protonation process and the addition of the metal, the reaction time decreased and the HGR increased. Also, the activity increased as the metal ratio increased from the ratio in the catalysts prepared by Bekirogullari (2020), DSCG-Zn, 50% Zn, and Selvitepe et al. (2019), Sepiolite-H_3PO_4-CoB, 50% Co. Subsequent experiments were continued with 50% Co^{2+}, which was the best metal ratio.

Effect of burning temperatures

The effect of the burning temperature of the DSCG-Co-Cat catalyst on the catalytic activity is shown in Fig. 3. The DSCG-Co-Cat catalyst was burned at different temperatures (300, 400, 500, and 600 °C) for 60 min. The reaction time of the catalyst was 2.5 min at 400 °C, which was the best burning temperature, while it was 7.5, 5.5, and 6.5 min at 300, 500, and 600 °C, respectively. As can be seen in the curve, the hydrogen generation time increases after 400 °C, so the HGR started decreasing after 400 °C. It has also been reported that catalytic activity decreased after 300 °C in other studies of DSCG and SCG (Kaya 2020b, 2020a).

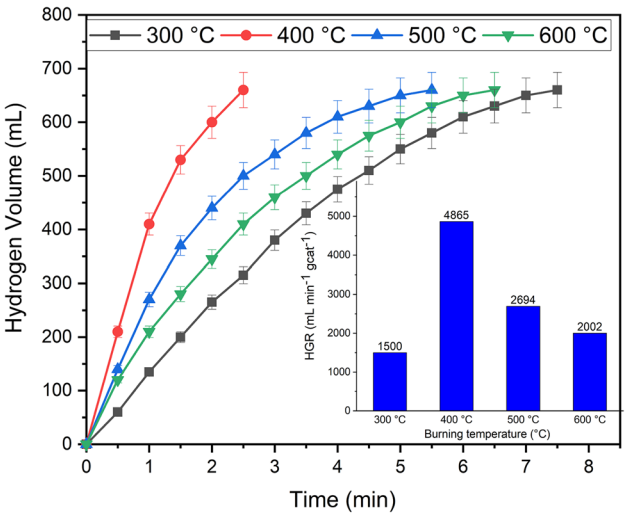


Fig. 3 Time-dependent change of HGR at different burning temperatures (reaction conditions: 2.5% $NaBH_4$, catalyst = 0.1 g, T = 30 °C, and Vmethanol = 10 mL)

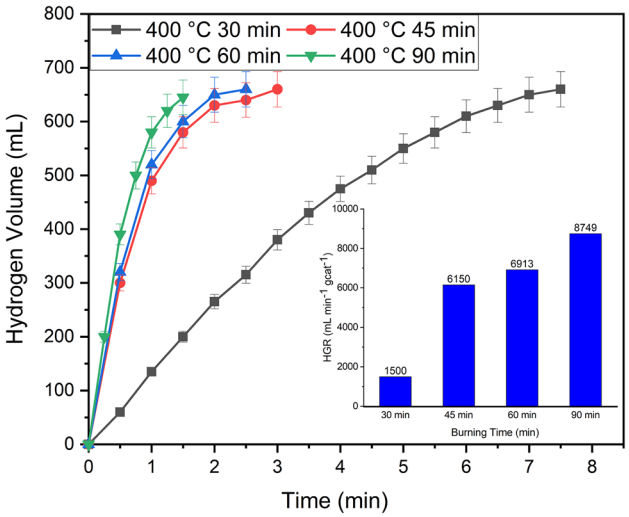


Fig. 4 Time-dependent change of HGR at different burning times (reaction conditions: 2.5% $NaBH_4$, catalyst = 0.1 g, T = 30 °C and Vmethanol = 10 mL)

Bekirogullari (2020) found the most active burning temperature to be 1000 °C in a DSCG-Zn catalyst. After determining the best temperature, the experiments were continued by investigation of the effect of the burning time.

Effect of burning times

The effect of different burning times on the activity of the DSCG-Co-Cat catalyst is shown in Fig. 4. The efficiency of the DSCG-Co-Cat catalyst burning at 400 °C was determined by trying four different burning times. The reaction decomposition time of the solution containing 2.5% $NaBH_4$ was completed in 1.75 min with the DSCG-Co-Cat catalyst burning at 400 °C for 90 min, and the reaction was completed in 2.5, 7.5, and 2.15 min when burned for 30, 45, and 60 min, respectively. Thus, the DSCG-Co-Cat catalyst that burned at 400 °C for 90 min showed superior results. Experiments continued with tests of the amount of the catalyst, the amount of $NaBH_4$, and the effect of temperature, as well as usability tests.

Effect of the catalyst amount

Figure S4 shows the change in the HGR for different amounts of DSCG-Co-Cat at the same temperature and $NaBH_4$ concentration. For catalyst amounts of 0.05, 0.1, 0.15, and 0.25 g, respective reaction completion time was 3.3, 1.8, 1.4, and 1 min and HGR was 10,806, 8749, 7543, and 5644 mL min^{-1} $gcat^{-1}$. As a result, we conclude that this was a catalyst-controlled reaction, and the reaction completion time for methanolysis of sodium borohydride decreases as the amount of catalyst increases.

Effect of the amount of $NaBH_4$

The effect of various $NaBH_4$ concentrations on the DSCG-Co-Cat catalyst was investigated, and the findings are presented in Fig. S5. Reaction time, reaction rate, and the amount of hydrogen produced were observed to increase when the concentration of $NaBH_4$ was increased from 1 to 5% by weight, thought when the amount of $NaBH_4$ was set as 7.5% by weight, HGR decreased. It is possible to say that this is because as the amount of $NaBH_4$ increases, the increase in viscosity of the solution deactivates the active sites (Kaya et al. 2014; Kaya 2020b).

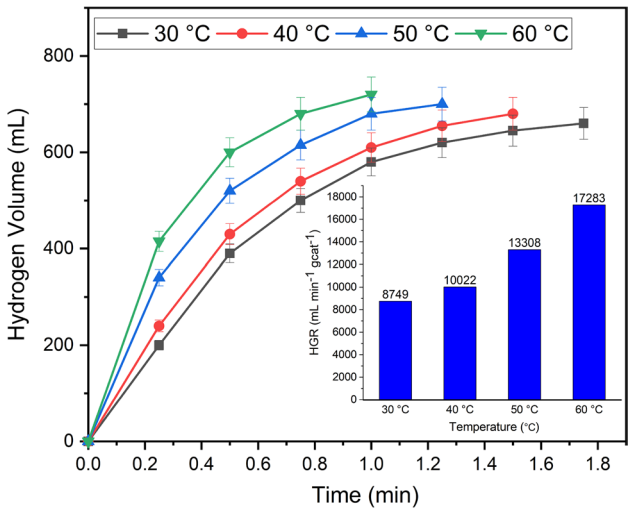


Fig. 5 Time-dependent change of HGR at different temperatures (reaction conditions: 2.5% $NaBH_4$, catalyst = 0.1 g, T = 30, 40, 50, 60 °C, Vmethanol = 10 mL)

Effect of temperature

The experiments in this study were carried out at four different temperatures (30, 40, 50, and 60 °C) to investigate the efficiency of the 0.1 g DSCG-Co-Cat catalyst in the methanolysis. The results of the temperature experiments, in terms of hydrogen volume against reaction time, are given in Fig. 5. The reaction at 60 °C was completed in 1 min, while the reaction at 30 °C was completed in 1.8 min. Therefore, we conclude that the temperature rise shortens the reaction time by increasing the rate of catalyst-controlled sodium borohydride decomposition. Meanwhile, the maximum HGRs for 30, 40, 50, and 60 °C were 8749, 10,022, 13,308, and 17,283 mL min^{-1} $gcat^{-1}$, respectively. In the methanolysis of 2.5% $NaBH_4$ catalyzed by 0.1 g of the DSCG-Co-Cat, the reaction rate at 30 °C was 8749 mL min^{-1} $gcat^{-1}$, while HGR of a raw metal-free DSCG catalyst (Kaya 2020b) used in the methanolysis of $NaBH_4$ is 3171.4 mL min^{-1} $gcat^{-1}$ in the literature. In this study, when the HGRs of the DSCG-Co-Cat catalyst prepared by the addition of a cheap metal to DSCG were compared, the reaction rate of the DSCG-Co-Cat catalyst was approximately 2.7 times faster than that of the DSCG.

The Arrhenius equation in Eq. (2) was used to calculate the activation energy of the $NaBH_4$ methanolysis catalyzed by the DSCG-Co-Cat. The kinetic curve of the DSCG-Co-Cat catalyst is shown in Fig. S6. The activation energy calculated from the slope of this curve was found to be 23.2 kJ mol^{-1}. Table 2 shows that this activation energy is lower than that of other metal-free and metal-containing catalysts, which is good because the lower the activation energy for a reaction, the higher the rate. Thus, catalysts speed up reactions by lowering the activation energy. According to

Table 2 Comparison of the maximum HGR and activation energies of metal- and non-metal-containing catalysts with other studies in the literature

Catalyst	Temperature (°C)	Maximum HGR (mL min^{-1} $gcat^{-1}$)	Ea (kJmol^{-1})	Refs
CoB	60	1640	44.5	Krishnan et al. (2009)
CoB/TiO_2	30	12,500	51	Lu et al. (2012)
CoB/Al_2O_3	30	11,650	56.80	Lu et al. (2012)
CoB/cat. supported on carbon black	30	10,821.6	56.72	Baydaroğlu et al. (2014)
CoB/cat. supported on carbon	30	3903.2	57.8	Zhao et al. (2007)
CoB/MWCNT	30	5110	40.4	Huang et al. (2008)
Co–Ni-P	30	3636	38	Guo et al. (2013)
Co–Ni-B	30	1175	34	Patel et al. (2010)
CoB/cat. supported on C. Vulgaris microalgal strain	30	13,215	25.22	Bekiroğulları et al. (2019)
SCG	30	8335.5	52.96	Kaya (2020a)
DSCG	30	3171.4	25.23	Kaya (2020b)
DSCG-Co-Cat	30	8567.9	23.2	This study

these results, the DSCG-Co-Cat catalyst is active and cost-effective for the methanolysis of $NaBH_4$.

Reusability of the DSCG-Co-CatReusability of the DSCG-Co-Cat

To test its reusability, the DSCG-Co-Cat catalyst was tested five times at 30 °C in methanolysis containing 2.5% $NaBH_4$, and the results are given in Fig. S7. The effect of the DSCG-Co-Cat catalyst decreased gradually after each use. The reason for this condition may be the formation of inadequate catalytic active sites for the methanolysis of $NaBH_4$ due to the loss of the catalyst, which may occur during washing and recycling. Another reason may be the increased sodium tetramethoxyborate concentration in the solution owing to the degradation of $NaBH_4$ during methanolysis. Still another may be a rise in the viscosity of the solution, which may lead to a reduction in the catalytic performance (Krishnan et al. 2009).

Electrochemical characterization of the DSCG-Co-Cat catalyst material as a supercapacitor electrode

The electrochemical properties of supercapacitors made from DSCG-Co-Cat material were obtained through CV, EIS, and GCD. The CV curves of the supercapacitor at 60 mV/s, 40 mV/s, 20 mV/s, and 10 mV/s scanning speeds are shown in Fig. 6a. The obtained curves were quasi-rectangular and near ideal supercapacitor curves. The quasi-rectangular shape of the CV curves indicated the presence of electrical double-layer capacitance. Noticeable redox peaks showing pseudocapacitance contribution were not observed. CV curves moved away from the rectangular structure as the current density increased at high scanning speeds.

The EIS analysis of the supercapacitor was carried out in a frequency range of 1 Hz to 30 kHz with an amplitude of 5 mV, and the results are displayed in Fig. 6b. The equivalent series resistance of the electrode was gauged to be as low as approximately 0.4 Ω. This small resistance indicates that the electrodes [± can be used to] transmit power at high levels (Cheng et al. 2011; Yan et al. 2014). No semicircles were seen in the high-frequency region corresponding to the load transfer resistance. This implies that electrodes have a prominent charge transfer ability. The slope of the impedance curve was low at low frequencies. This indicates that it is difficult for electrolyte ions to leak into the electrode material's pores, and thus, the diffusion resistance was high (Gamby et al. 2001; Zhu et al. 2018).

The charge–discharge curves of the supercapacitor at the 0.5 A/g, 1 A/g, and 2 A/g current densities are given in Fig. 6c. At the start of the discharge process, no significant voltage drop was observed because of the small electrode internal resistance (Song et al. 2019). Due to diffusion resistance, the curves diverged slightly from the shape of a twin-sided triangle which resembles the ideal supercapacitor curve.

The capacitance of the electrodes was calculated as 46 F/g for 2 A/g, 67 F/g for 1 A/g and 88 F/g for 0.5 A/g. The biomass material type, the pore structure of the material, the activation agent, the activation method, the additive material, the combustion temperature, and the electrolyte type determine the capacitance of the electrodes.

When the capacitance value of the DSCG-Co-Cat electrode is compared with that of biomass electrodes made from various banana fibers (Subramanian et al. 2007), coconut shells (Xia et al. 2018), pine cone biomass (Manyala et al. 2016), pine tree powder (Wang et al. 2017), waste shaddock endotheliums (Yang et al. 2016), rice husks (Zhang et al. 2017), and green onion leaves (Yu et al. 2016), promising capacitive results were obtained for supercapacitors by using metal-added coffee waste. Furthermore, better capacitive values can be acquired by preparing the active material at high temperatures with additives (Inal and Aktas 2020).

Future works

The study done is an environmentally friendly and sustainable approach in terms of the production of value-added products from waste materials. For the first time, by using the DSCG, which is one of the most abundant organic waste materials in nature, a catalyst was prepared by using cheaper cobalt metal instead of precious metals such as Pt and Ru in order to obtain higher yields in the methanolysis reaction of sodium borohydride. Additionally, by using this a catalyst material, a supercapacitor cell was designed for energy storage. Therefore, it is thought that this multifunctional "cap-cat" material produced by Co-doped waste coffee will constitute an important element in a hybrid system which includes capacitor and catalyst systems that can be installed in the future. The primary purpose of using this hybrid system is to produce hydrogen using an environmentally friendly catalyst. When hydrogen production is not needed, energy is stored by using this catalyst as a supercapacitor. In this way, continuity in the power system is ensured and the stored energy is transmitted back when necessary.

Conclusion

In the present study, the DSCG-Co-Cat catalyst was prepared by treating DSCG with 1 M CH_3COOH and Co^{2+} at different ratios and used to obtain hydrogen in methanolysis reactions with $NaBH_4$. The most active DSCG-Co-Cat

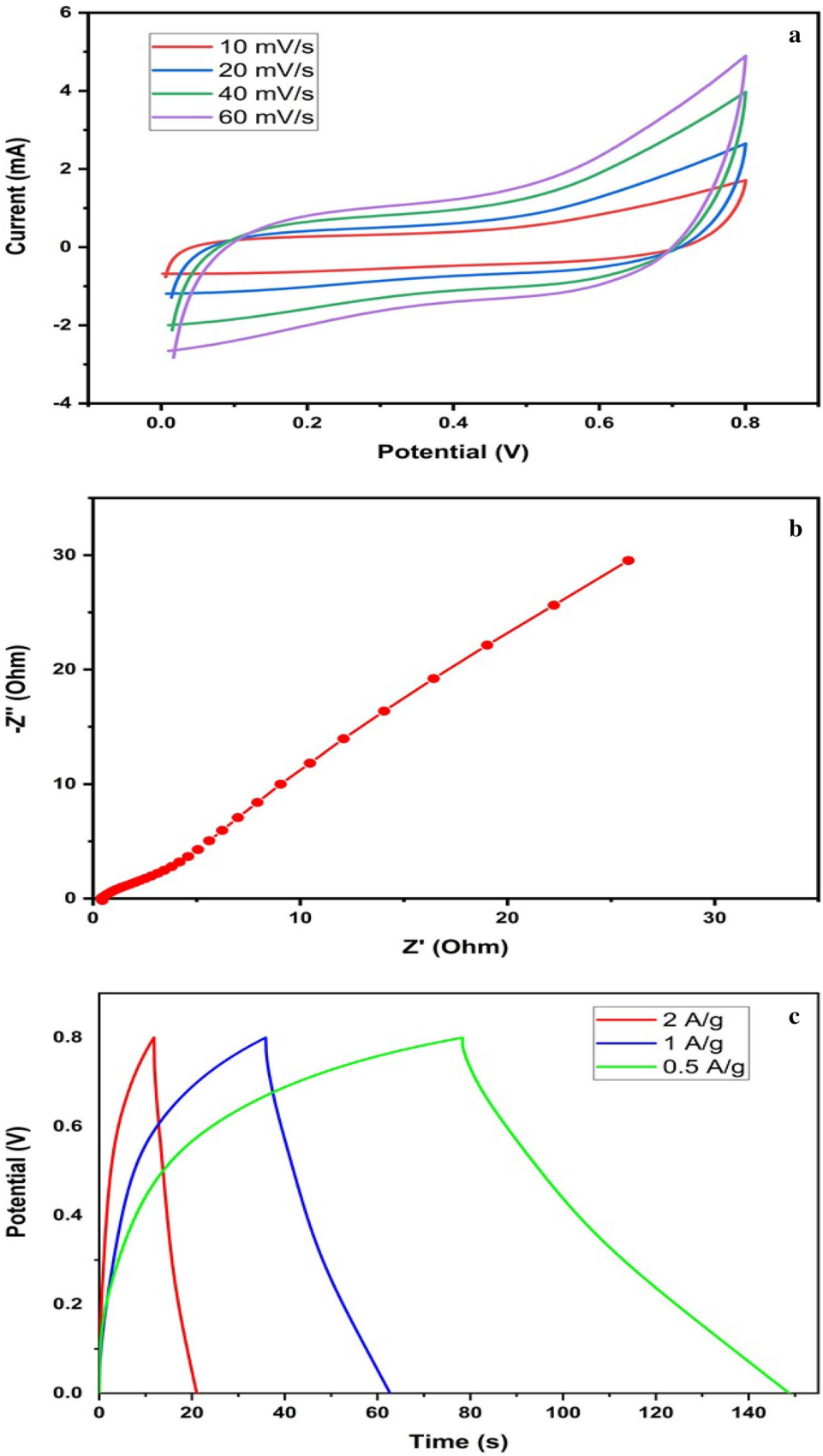


Fig. 6 CV curves of the supercapacitor **(a)**, impedance curve of the supercapacitor cell **(b)** and GCD curves of the capacitor cell at various current densities **(c)**

catalyst was obtained by burning at 400 °C for 90 min after the addition of 50% Co^{2+}. In a methanolysis of 2.5% $NaBH_4$ catalyzed by 0.1 g of DSCG-Co-Cat, the reaction rate at 30 °C was 8749 mL min^{-1} $gcat^{-1}$. The activation energy of the DSCG-Co-Cat catalyst was 23.2 kJ mol^{-1}. The reusability experiments were repeated five times under the same conditions, and nearly 100% conversion was achieved in each use. This indicates that adding cheap metal to waste is an important step in the production of high efficiency catalysts. Gravimetric capacitance of the supercapacitor electrode prepared using catalyst material was obtained by using GCD curves as 67 F/g at the current density of 1 A/g. The DSCG-Co-Cat material performed well both in hydrogen production when used as a catalyst and in energy storage when used as supercapacitor electrode material.

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