Synthesis of CaCr$_2$O$_4$/Carbon nanoplatelets from non-condensable pyrolysis gas of plastics for oxygen reduction reaction and charge storage

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ABSTRACT

An integrated pyrolysis and chemical vapor deposition using CaCr$_2$O$_4$ as a precursor were applied to convert mixed plastics into a nanocomposite comprising CaCr$_2$O$_4$ and carbon nanoplatelets (CaCr$_2$O$_4$/CNPs). During pyrolysis, plastics were decomposed into oil and non-condensable gas. While reacting with the precursor, non-condensable pyrolysis gas containing hydrocarbons and H$_2$ played a dual role: (1) provided carbon for nanoplatelets growth and (2) facilitated reduction of Cr(VI) to Cr(III). Cyclic voltammetry demonstrated the synergistic effect of CaCr$_2$O$_4$ and CNPs on the heterogeneous electron transfer rate. The nanocomposite showed good performance as an electrocatalyst for oxygen reduction reaction increasing current density and reducing overpotential to $-0.27$ V vs Ag/AgCl (sat.) at 0.06 mA cm$^{-2}$. Furthermore, the nanocomposite exhibited a specific electrochemical capacitance as high as 60 F g$^{-1}$ at 2 A g$^{-1}$ and 67% stability over 3000 cycles, demonstrating the capability of electrode for fast charge/discharge, long cycling life and high reversibility.

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1. Introduction

Transition metal oxides have been widely explored as electrode materials for energy storage devices and fuel cells. Due to electrochemical pseudocapacitance originating from redox reactions occurring at the metal oxide–electrolyte interface, transition metal oxides have high theoretical specific electrochemical capacitances compared to carbon materials and its derivatives (e.g., 1370 F g$^{-1}$ for MnO$_2$, 3560 F g$^{-1}$ for Co$_3$O$_4$, 2584 F g$^{-1}$ for NiO against 526 F g$^{-1}$ of graphene) [1–4]. Owing to the low-cost and high availability, transition metal oxides have been also investigated for the possible application in electrocatalysis, instead of relatively expensive precious metals [5,6]. Nanostructured oxides of Mn, Ni, Co, Fe and other metals were reported to catalyze oxygen reduction (ORR) and evolution (OER) reactions [5,6]. ORR plays an essential role as a cathodic half-cell in proton exchange membrane fuel cells [7], while OER is an important half-cell reaction for water splitting [8]. Furthermore, both OER and ORR are employed in rechargeable air-metal batteries [9], which have three to thirty times greater energy density than those of lithium-ion batteries and can potentially be used as energy storage devices [10]. The high electrochemical capacitance and the performance of metal oxides as electrocatalysts, however, are limited by the low electrical conductivity and the particle agglomeration. Binary metal oxides and metal oxide–carbon composites were reported to exhibit better electrochemical performance compared to single metal oxides, which is attributed to the changes in chemical composition, such as introduction of oxygen vacancies and incorporation of conductive carbon materials [4,6,10].

For electrochemical applications, the promising types of binary oxide systems are metal chromite spinels as they possess high chemical stability and can be used either directly or as a composite with carbon based materials [11–14]. NiCr$_2$O$_4$ synthesized by co-precipitation of Ni (II) and Cr(III) salts have demonstrated high performance as an electrode material for an electrochemical supercapacitor application [11]. Nanocomposites containing CoCr$_2$O$_4$ and carbon nanosheets grown by a facile one-step molten salt calcination method have exhibited good electrocatalytic activity and durability during OER [12]. ZnCr$_2$O$_4$ and multi-walled carbon nanotubes composite synthesized using hydrothermal method followed by calcination at 500 °C showed good performance as an enzyme-free sensor for monitoring H$_2$O$_2$ content in aqueous solutions [13]. MnCr$_2$O$_4$/Mn$^{4+}$/Mn$^{6+}$/O$_2$/carbon and CoCr$_2$O$_4$/...
carbon nanocomposites prepared by annealing of Mn—Cr and Co—Cr coordination compounds at 350 °C in air, respectively, demonstrated high specific electrochemical capacitance [14].

Despite the proof that transition metal chromites either independently or as composites with carbon nanostructures can serve as high performance electroactive materials, there is lack of evidence regarding the performance of non-transition metal chromites. To address this issue, in the present work, a novel composite comprising CaCr2O4 and carbon nanoplatelets (CaCr2O4/CNPs) was synthesized and tested. Two stage thermal process was applied for the synthesis of the nanocomposite material. In the first stage, plastic mixture, simulating the composition of mixed plastic waste, was converted into oil and non-condensable pyrolysis gas. While oil can be utilized in boilers and internal combustion engines, non-condensable pyrolysis gas (representing 10–90% of product yields [15,16]) is typically burnt [17]. Upcycling of non-condensable pyrolysis gas into carbon-based electrode materials can substantially reduce the carbon footprint of plastic pyrolysis and serve as a source of hydrocarbons for the synthesis. Therefore, in the second stage, non-condensable pyrolysis gas was converted via chemical vapor deposition into carbon nanostructures over the chromium containing precursor. The produced nanocomposite was characterized using voltammetry and electrochemical impedance spectroscopy to investigate heterogeneous electron transfer, and applied as an electrode using voltammetry and electrochemical impedance spectroscopy to investigate the performance of the electroactive materials, there is lack of evidence regarding the performance of non-transition metal chromites. To address this issue, in the present work, a novel composite comprising CaCr2O4 and carbon nanoplatelets (CaCr2O4/CNPs) was synthesized and tested. Two stage thermal process was applied for the synthesis of the nanocomposite material. In the first stage, plastic mixture, simulating the composition of mixed plastic waste, was converted into oil and non-condensable pyrolysis gas. While oil can be utilized in boilers and internal combustion engines, non-condensable pyrolysis gas (representing 10–90% of product yields [15,16]) is typically burnt [17]. Upcycling of non-condensable pyrolysis gas into carbon-based electrode materials can substantially reduce the carbon footprint of plastic pyrolysis and serve as a source of hydrocarbons for the synthesis. Therefore, in the second stage, non-condensable pyrolysis gas was converted via chemical vapor deposition into carbon nanostructures over the chromium containing precursor. The produced nanocomposite was characterized using voltammetry and electrochemical impedance spectroscopy to investigate heterogeneous electron transfer, and applied as an electrode using voltammetry and electrochemical impedance spectroscopy (EIS), and charge/discharge (CD) measurements by chronopotentiometry were conducted using Interface 1000 Potentiostat (Gamry, USA) equipped with a three-electrode electrochemical cell (the working surface area of 0.07 cm²). 0.05 M ethanol were used to modify GC electrodes. For electron transfer from N2 adsorption data applying the BET model and quenched solid density functional theory (QSDFT) equilibrium model, which takes into account heterogeneity of surface of carbonaceous materials [18]. QSDFT modeling was conducted assuming slit pore geometry of carbons in nanocomposite.

2.2. Characterization of material structure

The materials were characterized using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) equipped with the energy dispersive X-ray spectroscopy (EDS, Oxford Xmax80 LN2 Free), transmission electron microscopy (TEM, JEOL JEM-1400 and JEM-2010), X-ray diffraction analysis (XRD, Bruker AXS DB Advance), Raman spectroscopy (XploRA PLUS with a 532 nm laser, Horiba Scientific), X-ray photoelectron spectroscopy (XPS, Kratos Axis Supra) and N2 adsorption and desorption isotherms at −196 °C (Quantachrome Autosorb-1 Analyzer). Specific surface area and pore size distribution were calculated from N2 adsorption data applying the BET model and quenched solid density functional theory (QSDFT) equilibrium model, which takes into account heterogeneity of surface of carbonaceous materials [18].

Temperature programmed oxidation was conducted in a thermogravimetric analyzer STA 449 F3 Jupiter (Netzsch Group). 10 mg of nanocomposite was loaded into an Al2O3 crucible, dried in air (250 mL min⁻¹) at 105 °C to remove moisture and then heated in air at to 1000 °C (15 °C min⁻¹).

2.3. Electrochemical testing

NN-dimethylformamide (DMF), potassium ferrocyanide trihydrate [KFe(CN)₆·3H₂O], potassium ferricyanide [K₃Fe(CN)₆], potassium dichloride, potassium hydroxide, 20 wt% platinum on graphitized carbon and concentrated sulphuric acid (95–98%) were purchased from Sigma Aldrich.

All electrochemical measurements, namely, cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and charge/discharge (CD) measurements by chronopotentiometry were conducted using Interface 1000 Potentiotstat (Gamry, USA) equipped with a three-electrode electrochemical cell consisted of a Pt mesh as a counter electrode, Ag/AgCl/KCl (sat.) (ALS, Japan) as a reference electrode and a glassy carbon (GC) disk as a working electrode (CH Instruments, USA) (the working surface area of 0.07 cm²). 0.05 μm alumina and micropolishing pad were obtained from ALS, Japan. The electrodes were received and were not recalibrated. All electrochemical experiments were performed at ambient temperature (24–25 °C) in a voltammetric cell (5 mL) with no agitation. The electrolyte was bubbled with air and N2 for 20 min to reach air-saturation and N2-saturation, respectively. Before the usage, the GC electrodes were polished using 0.05 μm polishing alumina slurry on a polishing pad and rinsed with absolute ethanol followed by washing with ultra-high quality (UHQ) water. Two different approaches were used for the preparation of CaCr2O4/CNPs dispersions which were used to modify GC electrodes. For electron transfer
characterization by CV and EIS in mild conditions, specifically, in 5 mM potassium hexacyanoferrate (III)/(II) (Fe(CN)₆³⁻/⁴⁻) containing 100 mM KCl, 1 mg mL⁻¹ of CaCr₂O₄/CNPs were dispersed in chitosan solution (0.1% of chitosan in acetic acid) using a probe sonicator with a diameter of 3 mm as described elsewhere [19]. Sonication was performed for 2 min using 3 s pulses with 1 s intervals at amplitude of 20%. GC electrodes were modified by drop-casting two portions of 3 μL of CaCr₂O₄/CNPs dispersion on a GC electrode. The second drop was added after 30 min, making sure the first drop had dried. CVs were performed at 50 mV s⁻¹ scan rate from −0.2 to 0.6 V. Five cycles were measured and the second cycle was chosen as the representative one due to the negligible differences between the data obtained during second and fifth cycles. EIS was carried out in the frequency range from 0.1 Hz to 100 kHz at an open circuit potential with an alternating current amplitude of 10 mV. Open circuit potential was stabilized for 10 s.

Oxygen reduction reaction (ORR) and specific electrochemical capacitance (EC) evaluation were performed using 0.1 M KOH and 1 M H₂SO₄ solutions, respectively. For these tests, the second dispersion protocol described by Maharjan et al. was employed to modify GC electrode with CaCr₂O₄/CNPs [20]. 5 mg mL⁻¹ of the CaCr₂O₄/CNPs were dispersed in N,N-dimethylformamide and sonicated in an ultrasound bath for 30 min to obtain a homogeneous dispersion. 1 μL of the dispersion was deposited on a GC electrode and dried under an incandescent lamp for 10 min. ORR tests were performed by LSV (sweeping rate 100 mV s⁻¹), while Ca(OH)₂ is formed from CaO and moisture in air during handling and XRD analysis. During calcination, Cr(III) was oxidized to Cr(VI) as suggested by the formation of CaCrO₄. Similar results were reported when chromium(III) nitrate was used for the synthesis of chromium-based catalysts supported on Al₂O₃ [22]. At loadings up to 9% by mass, CrO₃ was the dominant chromium species while at higher loadings CrO₂ was partially reduced to Cr₂O₃. Due to the acidic nature, CrO₃ can react with calcium compounds during the calcination stage producing CaCrO₄.

The yields and ultimate analyses of nanocomposites prepared at three synthesis temperatures are summarized in Table 1. An increase in synthesis temperature from 500 to 700 °C increased the yield of produced nanocomposite material nearly 2.3 times from 6.2 to 14.1% per Cr—Ca mass. The ultimate analysis confirmed the presence of 8.5–13.6% C and 1.2–2.9% H in the synthesized materials (depending on the temperature of chemical vapor deposition), while N content was negligible. To identify the type of hydrocarbon compounds in the non-condensable pyrolysis gas acting as precursors for carbon deposition over Cr—Ca, the C₁—C₅ gases and C₆+ hydrocarbons were analyzed by GC and GC–MS, respectively. Fig. 2a depicts the volumes of C₁—C₅ hydrocarbons and H₂ in the non-condensable pyrolysis gas after the treatment in the absence and presence of Cr—Ca at 700 °C (i.e. at the temperature that resulted in the highest yield of nanocomposite material). Both gases contained substantial quantities of methane, ethane, propane, ethylene, propylene and C₄ alkenes. Traces of other compounds, such as C₄ and C₅ alkanes, dienes and acetylenes, were also present. The total yields of collected C₁—C₅ hydrocarbons produced during pyrolysis of plastic mixture after the treatment in the presence and absence of Cr—Ca were 14.8 ± 0.7 and 15.0 ± 1.1% per mass of feedstock, respectively (the data are presented as averages ± standard deviations of three runs). The differences in the volumes of hydrocarbon gases were also within the statistical error, indicating that there was no significant decomposition of C₁—C₅ hydrocarbons. On the other hand, after the gas treatment in the presence of Cr—Ca, the volume of H₂ increased, suggesting the deposition of carbon from other carbonaceous precursors via the following reaction:

\[ \text{C}_x\text{H}_y = x\text{C} + 0.5y\text{H}_2 \] (2)

Since no decomposition of C₁—C₅ hydrocarbons was observed, C₆+ hydrocarbons were the most likely precursors. Fig. 2b shows a representative GC–MS chromatogram of isopropanol solution collected in the absence of Cr—Ca at 700 °C. 13 peaks with retention times between 2.8 and 7.5 min were observed and are attributed to C₆+ hydrocarbons, one of which is the internal standard (i.e. toluene d₈) added for quality control. The assignment and decomposition of these compounds in the presence of Cr—Ca at 700 °C are summarized in Table 2. All the identified species were cyclic hydrocarbons (aromatic and non-aromatic) containing double carbon bonds. Benzene and toluene were the most stable species and did not decompose over Cr—Ca. The decomposition of other species was between 11 and 100%, explaining the release of H₂ and formation of carbon in the nanocomposites.

### Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Yield (wt%)*</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
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<td>700</td>
<td>14.1</td>
<td>11.1</td>
<td>1.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Calculated as (mass of nanocomposite after HCl washing/mass of Cr—Ca) × 100%.
3.2. Structure of CaCr$_2$O$_4$/CNPs

The physicochemical and electrochemical properties of the nanocomposite synthesized at 700 °C were characterized as the material produced at this temperature had the highest yield. Fig. 3a depicts the temperature programmed oxidation profile. The loss of ~28% of mass during thermal treatment in air at temperatures between 270 and 470 °C was observed and is attributed to the partial combustion of the material (i.e. carbon). The mass of the remaining inorganic fraction (~72%) did not change significantly up to 1000 °C, indicating high resistance to oxidation of the formed CaCr$_2$O$_4$. The Raman spectra in Fig. 3b contains peaks at ~1350 cm$^{-1}$ (D-band) and 1580 cm$^{-1}$ (G-band) corresponding to deposited carbon [23]. The presence of both peaks indicates defective structure of the material and low graphitization degree, which are typical to many carbon materials synthesized via chemical vapor deposition technique [24–27]. The presence of both peaks indicates defective structure of the material and low graphitization degree, which are typical to many carbon materials synthesized via chemical vapor deposition technique [24–27]. The shoulder at 1100 cm$^{-1}$ corresponds to symmetric CO$_3^{−}$ stretching in metal carbonates [27]. This indicates that most likely, carbonate-ions are present as an impurity on the surface of material or were incorporated into the structure of nanocomposite upon synthesis due to the utilization of CaCO$_3$ support. The Raman peak at ~600 cm$^{-1}$ corresponds to vibrations in Cr$_3$O$_7^{2−}$ [28,29].

According to Fig. 3c, the nanocomposite has broad XRD peaks that could be attributed to α-CaCr$_2$O$_4$ spinel, which has the orthorhombic structure with Pmnn space group. In oxygen free atmosphere, the conversion of CaCrO$_4$ into CaCr$_2$O$_4$ starts above ~900 °C [30], which is ≥70°C higher that the temperatures utilized in this study. The lower temperature required for CaCr$_2$O$_4$ synthesis could be attributed to the presence of hydrocarbons and H$_2$ in the gas, which facilitate the reduction of Cr(VI) to Cr(III) [31]:

$$2\text{CaCrO}_4 + 3\text{H}_2 = \text{CaCr}_2\text{O}_4 + \text{CaO} + 3\text{H}_2\text{O}$$  

(3)

The absence of graphite peaks in XRD pattern at 27° and 43° (Fig. 3c) suggests non-crystalline structure of CNPs [32]. The small broad peaks emerging in the regions of 50–60° and 70–80° could be attributed to unidentified impurities, which have low crystallinity and/or present at low concentrations. Energy dispersive X-ray spectroscopy (EDS) spectrum confirms the presence of Ca and Cr in the synthesized nanocomposite (Fig. S2). Only traces of chlorine were identified in the sample, which can originate from chlorine species released during pyrolysis of PVC and/or from HCl used for acid washing. According to EDS, the atomic Ca:Cr ratio was 1:7.4, indicating that other non-crystalline chromium compounds can be present in the CaCr$_2$O$_4$/CNPs sample. As suggested by Cr 2p core level XPS spectrum (Fig. S3), Cr 2p3/2 had binding energy of 577 eV, corresponding to Cr(III) species [11]. According to N$_2$ adsorption isotherm shown in Fig. 3d, the nanocomposite is a porous material with total pore volume of 0.42 mL g$^{-1}$ containing both micro- (P/P$_0$ < 0.1) and mesopores (0.1 < P/P$_0$ < 0.95). The larger N$_2$ adsorption at P/P$_0$ > 0.1 suggests that mesopores predominate in the synthesized material. This is also evident from the pore size distribution (Fig. 3e) illustrating that the majority of pores is in the mesopore range between 2 and 16 nm. The specific surface areas of nanocomposite calculated using BET and QSDFT models are 120 and 136 m$^2$ g$^{-1}$, respectively, suggesting good agreement between the models used for the characterization of nanocomposite.

Fig. 4 illustrates FESEM and TEM images of the synthesized CaCr$_2$O$_4$/CNPs nanocomposite (700 °C). Two types of structures can be identified in the images. The major part of the nanocomposite comprises flat plates with thicknesses 4–25 nm as shown in Fig. 4a and b. Side views in Fig. 4c and d suggest that the plates consist of layered material with ordered arrangement of atoms and are probably attributed to CaCr$_2$O$_4$, which is the main crystalline compound in the nanocomposite. The thickness of layers in plates was approximately 0.6 nm (Fig. 4d). These plates are surrounded by the second type of material (Fig. 4e and f), which appears to be carbon and resembles the morphology of carbon nanoplatelets [33].

The data presented in Figs. 3 and 4 demonstrate that the proposed synthesis route is a viable method for fabrication of CaCr$_2$O$_4$/CNPs nanocomposites. Due to the facile preparation method of Cr—Ca and abundance of waste pyrolysis gas, the method is easily scalable for mass production. Since electrochemical properties of CaCr$_2$O$_4$ containing materials has not been previously investigated, electrochemical characterization of the prepared CaCr$_2$O$_4$/CNPs nanocomposite was carried out.
3.3. Electrochemical properties

Fig. 5a and b show the redox behavior of CaCr₂O₄/CNPs deposited on a GC electrode surface characterized by CV and EIS measurements using Fe(CN)⁶³⁻/⁴⁻ redox couple as a standard probe. In Fig. 5a, the comparison between CVs of bare GC (black curve) and CaCr₂O₄/CNPs-modified GC (red curve) electrodes is shown. The CV of CaCr₂O₄/CNPs is characterized with a cathodic peak at 0.184 V and an anodic peak at 0.283 V, corresponding to the reduction of Fe(CN)⁶³⁻ to Fe(CN)⁶⁴⁻ and the oxidation of Fe(CN)⁶⁴⁻ to Fe(CN)⁶³⁻, respectively. The CaCr₂O₄/CNPs-modified GC electrode exhibited narrowed peak to peak separation (ΔEpp), where it decreased from 0.124 to 0.099 V in CaCr₂O₄/CNPs as compared to GC, indicating better reversibility of heterogeneous electron transfer [34]. Furthermore, the comparison of the magnitude of the anodic and cathodic peak current densities of the bare GC and CaCr₂O₄/CNPs-modified GC electrodes clearly shows that the CaCr₂O₄/CNPs-modified GC electrode is characterized with higher redox current density, confirming improved heterogeneous electron transfer. Moreover, the higher charging density observed throughout the entire potential range (−0.2–0.6 V) shows the emerged electrochemical double layer capacitive behavior of CaCr₂O₄/CNPs-GC electrodes. EIS measurements (Fig. 5b) support the CV results showing decreased resistance of
heterogeneous electron transfer. Specifically, the Nyquist plot exhibits a lowered hemi-circle at a high frequency range, and accordingly, its extrapolation to $Z_{\text{real}}$ axis gives a smaller value in the intercept (red curve). It is well known that a hemi-circle size at high frequency range represents the heterogeneous electron transfer kinetics between an electrode surface and redox reactant in a solution phase, and its extrapolation to the $Z_{\text{real}}$ axis towards lower frequency range gives the sum of electron transfer resistance and electrolyte/system resistance [35]. The above qualitative electrochemical characterization shows a great prospect of CaCr$_2$O$_4$/CNPs to be used as a platform for electrochemical sensors, e.g. for hydrogen peroxide determination, with improved sensing characteristics as carbon nanotube films were previously been found offering efficient heterogeneous electron transfer for detection of hydrogen peroxide at low working potential [36]. In addition to the standard characterization of redox behavior, CaCr$_2$O$_4$/CNPs-modified electrodes were also tested for the oxygen reduction reaction (ORR). Fig. 5c shows ORR over the bare GC electrode (black curve), the GC electrode modified with CaCr$_2$O$_4$/CNPs (red curve), and GC electrode modified with CaCr$_2$O$_4$ (blue curve) after calcination of CaCr$_2$O$_4$/CNPs in air that was used to remove carbon. During the LSV measurements, the electrodes were submerged in air-saturated 0.1 M KOH solution. In the reference experiments, N$_2$-saturated 0.1 M KOH was used in order to ensure that the observed reduction peak occurred due to the ORR. It can be seen that during the ORR, both bare GC and CaCr$_2$O$_4$-modified GC electrodes demonstrated overpotential of $-0.38$ V vs Ag/Ag/KCl (sat.) at a similar current density, namely in the range of 0.040–0.043 mA cm$^{-2}$. CaCr$_2$O$_4$/CNPs-modified electrode showed reduced overpotential of $-0.27$ V vs Ag/Ag/KCl (sat.) at higher current density, that is 0.050 mA cm$^{-2}$. To compare the obtained results with the best known electrocatalyst for ORR, that is Pt, a commercial 20 wt % Pt on graphitized carbon (C/Pt) (yellow curve) was employed as a working electrode in ORR. C/Pt electrode expressed an onset potential of $-0.09$ V and a plateau current density of 0.068 mA cm$^{-2}$. Although, the performance of the commercial Pt electrocatalyst clearly outperformed the synthesized CaCr$_2$O$_4$/CNPs, yet the replacement of expensive Pt electrode by waste-derived carbon nanocomposites as an electrode material for electrocatalysis of ORR for application in fuel cells, is rather desirable.

Fig. 4. FESEM (a, b) and TEM (c–f) images of the prepared CaCr$_2$O$_4$/CNPs composite (700 °C).
CV measurements shown in Fig. 5a suggest the electrochemical capacitive nature of CaCr$_2$O$_4$/CNPs-modified GC electrode compared to the bare GC electrode. Since electrochemical double layer capacitance is not a Faradaic (redox) process and charging current is directly proportional to a potential scan speed, the series of CVs were performed using a wider potential range in acidic 1 M H$_2$SO$_4$ solution in the absence of redox couple at potential scan rates from 10 to 200 mV s$^{-1}$. The inset of Fig. 5d shows that both bare GC and CaCr$_2$O$_4$-modified GC electrodes exhibit no significant electrochemical capacitive behavior. Whereas for CaCr$_2$O$_4$/CNPs-modified GC electrodes, a significant charging current indicated an electrochemical capacitance nature. Moreover, some electrochemical pseudocapacitative behavior was also demonstrated since an oxidation peak was observed starting from 0.85 to the maxima at 1.2 V and a consequent reduction peak at 1 V. Previously, chromium oxide-type materials were used as electrodes in electrochemical supercapacitors in aqueous systems [21,37–42]. However, the efficiency of CaCr$_2$O$_4$ containing composites has not been investigated. When increasing the potential scan rate, the charging current density increased accordingly as expected for a double layer electrochemical capacitor (Fig. 5d). Obviously, the inclusion of a conductive carbon additive is necessary for the composite to exhibit good electrochemical capacitance [21,37–39]. In a recent work, Chen et al. demonstrated that Cr$_2$O$_3$/multi-walled carbon nanotubes based electrochemical supercapacitor operated within a limited potential window of $-0.05$ to 0.45 V in basic media of 1.0 M KOH against standard calomel electrode [38]. Separately, Lota et al. developed a chromium oxide-MWCNT electrochemical supercapacitor in acidic media with a relatively small potential window of 0 to 0.8 V in a 2 electrode system in 1.0 M H$_2$SO$_4$ [21]. An operation of a wide potential window is needed to achieve higher energy-density capabilities of the electrodes [43,44]. As such, the CaCr$_2$O$_4$/CNPs nanocomposite demonstrates promising behavior as an electrochemical supercapacitor in acidic media with a wide potential window of $-0.6$ to 1.2 V.

With increasing charge and discharge rates, the time for completion of 1 cycle decreases, as the charges are stored and then eventually expended at a faster rate. The response shows a non-ideal triangular shape due to a redox process, which is a typical electrochemical pseudocapacitance characteristic [45]. From the discharge curve, the corresponding electrochemical capacitance of the material was calculated using Eq. (1). At a discharge rates of 1, 2 and 5 A g$^{-1}$, the electrochemical capacitance of CaCr$_2$O$_4$/CNPs was maintained at relatively...
constant values of 60, 58 and 61 F g\(^{-1}\), respectively (Fig. 6b). This is higher than the electrochemical capacitance of 50 F g\(^{-1}\) reported for a composite containing Cr\(_2\)O\(_3\) and single walled carbon nanotubes at charge/discharge rate of 5 A g\(^{-1}\) [21]. In case of CaCr\(_2\)O\(_4\)/CNPs, the specific electrochemical capacitance of 50 F g\(^{-1}\) was maintained at the charge/discharge rate as high as 20 A g\(^{-1}\) (Fig. 6b), demonstrating the superior performance of the synthesized composite over other available chromium-based electrode materials. Besides the better performance, one advantage of CaCr\(_2\)O\(_4\)/CNPs is the simple and scalable synthesis method, which allows for the mass production of inexpensive nanocomposite for energy application as compared to single walled carbon nanotubes. A long-term charge-discharge of the electrode material for 3000 cycles at 2 A g\(^{-1}\) was used to determine the stability of the material at long-term cycling (Fig. 6c and d). Apart from the decrease in the electrochemical capacitance from 58 F g\(^{-1}\) to 45 F g\(^{-1}\) for the initial 100 cycles, the electrochemical capacitance of the CaCr\(_2\)O\(_4\)/CNPs remained relatively stable (i.e. between 40 and 45 F g\(^{-1}\)), demonstrating the capability of electrode to sustain long-term charge/discharge cycling and reversibility.

4. Conclusions

A novel nanocomposite consisting of α-CaCr\(_2\)O\(_4\) spinel plates bonded with CNPs (CaCr\(_2\)O\(_4\)/CNPs) was produced from mixed plastics using a two-stage pyrolysis and chemical vapor deposition process. The nanocomposite was characterized using CV and EIS measurements, showing that the electrochemical performance of material was related to synergistic interactions between two components (i.e. α-CaCr\(_2\)O\(_4\) and CNPs). The nanocomposite was applied as an electrocatalyst for ORR and as an electrode material for charge storage. During ORR in alkaline electrolyte, CaCr\(_2\)O\(_4\)/CNPs demonstrated electrocatalytic ability, increasing current density and decreasing overpotential. Furthermore, CaCr\(_2\)O\(_4\)/CNPs exhibited the specific electrochemical capacitance as high as 60 F g\(^{-1}\) at 2 A g\(^{-1}\) and presented 67% long-term cycling stability over 3000 cycles. High electrochemical capacitance values for CaCr\(_2\)O\(_4\)/CNPs were maintained over a wide potential window of 1.8 V, indicating the suitability of material for the application as an electrode material for charge storage in electrochemical supercapacitors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2019.113368.

References
