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Carbide-Derived Carbon by Electrochemical Etching of Vanadium Carbides

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Carbide-derived Carbon (CDC) has been demonstrated to be an excellent electrode material for electrochemical devices including supercapacitors due to its chemical and electrochemical stability, large specific surface area and controllable pore size and morphology. Currently, CDC is prepared from metal carbides by chlorination in a chlorine gas atmosphere at temperatures of 350°C or higher. In this paper, conversion using electrochemical methods is reported, which can be achieved by oxidizing vanadium carbides (VC or V₂C) in aqueous solutions at room temperature and a mild electrode potential to prepare CDC thin film as electrode materials for “on-chip” supercapacitors. It was found that VC and V₂C can both be oxidized at a potential of about 0.4 V vs. Ag/AgCl or higher in neutral, acidic, or basic solutions. After the oxidation, vanadium is readily detected in the electrolyte solutions by ICP-MS (Inductively Coupled Plasma – Mass Spectrometry). The so-produced CDC thin film electrode (ca. 2.0 - 2.6 μm thick) has a porous morphology and bears specific double layer capacitance values as high as 0.026 F.cm⁻² (or 130 F.cm⁻³) with some dependence on the oxidation potential, time, and electrolyte solutions.

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Carbide-Derived carbon (CDC) is a new type of porous carbon material demonstrating high purity, a narrow distribution of pore sizes, and significant specific surface area.^{1,2} Due to these unique properties, CDC was found to be very useful for gas storage, flow sensors, and as an electrode material for electrochemical energy storage devices such as supercapacitors.^{3–7} Currently, the most reliable method to synthesize CDC is to remove the metal or metalloid elements selectively from binary or ternary carbide precursors.^{1,8,9} This has been achieved by chlorine gas treatment (chlorination) at a temperature of 350°C or higher. At an elevated temperature, metal / metalloid elements can be reacted to be volatile metal chlorides and purged using an argon gas stream. Thus, the left-over carbon is metal free and sp² or sp³ hybridized. To date, CDC has been successfully synthesized from binary carbides such as TiC, Cr₃C₂, Fe₃C, Mo₂C, Nb₂C, SrC₂, Ta₂C, VC, V₂C WC, W₂C, ZrC, as well as ternary carbides (also called MAX phase carbides) such as Ti₂AlC, Ti₃AlC₂. Most of this work has been performed in bulk solids/powders. Depending on the crystalline/elemental structure of the precursor and the reaction temperature, the pore size of CDC can be controlled in the range over 2–50 nm.¹ The theoretical bulk porosity is between 50–90% in volume. Thus far, the Cl₂ reaction method of etching has been primarily used but one downside is that the Cl₂ gas is toxic, corrosive and the process itself is relatively expensive. On the other hand, an alternative oxidation method is to prepare CDC under more environmentally favorable conditions that have been rarely explored. For example, Y. Gogotsi and coauthors reported the electrochemical etching of MAX-phase carbides to produce CDC at room temperature using HF, HCl, or NaCl electrolyte solutions at potentials higher than 0.5 V vs. Ag/AgCl, in HF, or 2.0 V, in HCl.¹⁰

In this paper, we report, for the first time, an electrochemical oxidation of textured binary monolithic vanadium (IV) carbide (VC) and vanadium (II) carbide (V₂C) thin films on either electrically conducting or insulating substrates. Vanadium metal was readily oxidized and removed from the carbide crystal and dissolved in the electrolyte solutions when the electrode potential was ramped to be 0.4 V vs. Ag/AgCl or higher. This oxidation can occur when the VC or V₂C thin films were deposited on either a conductive substrate, such as glassy carbon, or on an insulating substrate, such as sapphire. The so-produced CDC on substrate is porous and bears significant double layer capacitance of as high as 0.026 F.cm⁻² (130 F.cm⁻³), which

makes it a promising material for electrodes of “on-chip” supercapacitors or other purposes. The electrochemical etching of the carbides uses non-toxic aqueous solutions at room temperature and at relatively low over potentials. This is an energy-saving, time-saving, and environmental friendly method of CDC synthesis.

Further, in this work, the electrochemical etching is performed on highly textured binary carbide thin films. Textured films provide high quality precursor materials that allow more control in the process converting them to CDC since the conversion takes place through the same crystallite face only differing near grain boundaries. The textured films can be epitaxial, so each grain/crystallite is converted in the same way possibly resulting in a very narrow distribution of pore sizes. It has been reported that the specific capacitance of CDC thin-film devices exceeds that of their bulk counterparts by a factor of 2 or greater.¹¹

Materials and Methods

Binary carbide precursors were synthesized using a reactive magnetron sputtering approach on substrates of glassy carbon or sapphire. A high-purity target (99.5%) of vanadium metal (Lesker, Inc.) was used in two-inch circular planar magnetron cathodes in a specially designed three-target turbo-pumped UHV system. Two mass-flow controllers (MFC) were used to introduce gases into the system allowing the introduction of the sputtering gas, argon (Ar), and the reactive gas, acetylene (C₂H₂). The system is configured with a residual-gas analyzer (RGA) which allows a measurement of the ratio of Ar to C₂H₂ as well as ensuring that nitrogen, oxygen and water vapor contents are sufficiently low so that they do not cause a problem leading to the formation of metal oxides and nitrides during the deposition and that the background gases are at consistent levels. The base pressure of the chamber is 2 × 10⁻⁸ torr and the pressure in the chamber during sputtering was 0.010 torr. This pressure is controlled using a baffle valve to throttle the pumping speed. Temperature is controlled up to 900°C throughout the deposition process using a non-inductive molybdenum metal resistive heater approximately 2.5 cm below the substrate holder. The temperature is measured using a type-K thermocouple located below the heater and calibrated against a pyrometer reading of the film surface. The final carbide film thicknesses were in the range of 0.5 – 3 μm, depending on time of deposition.

The vanadium carbide (VC or V₂C) coated substrates were used as the working electrodes in the electrochemical measurements. The

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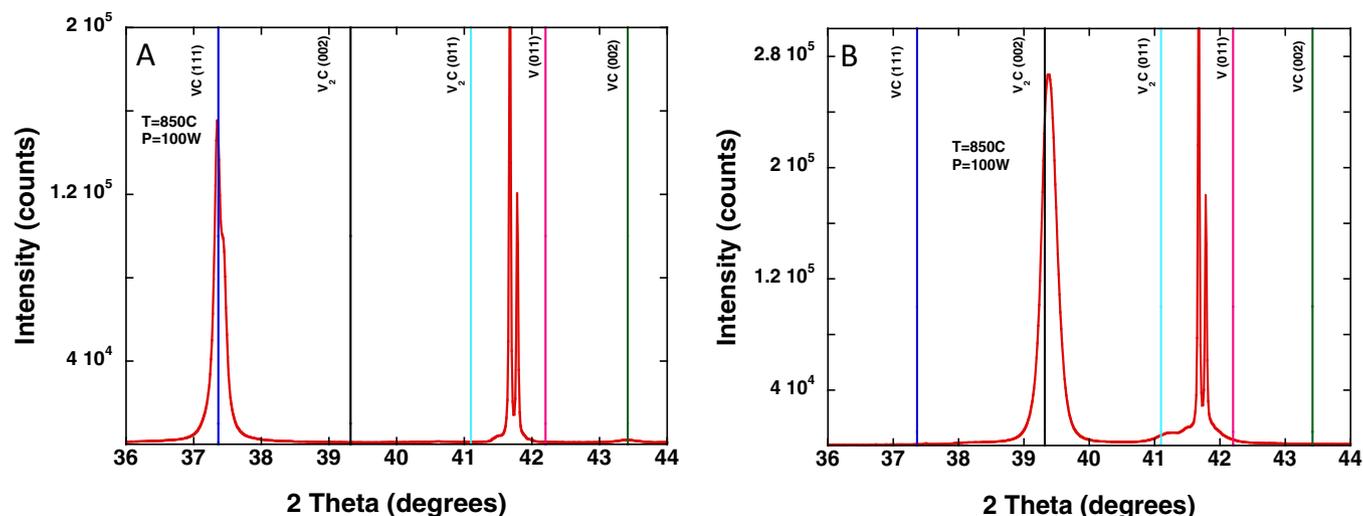


Figure 1. XRD pattern for textured VC (A) and V_2C (B) films grown at 850°C with a pulsed DC power supply at 100 W and with an acetylene flow of 0.80 sccm for the VC and 0.60 sccm for the V_2C .

working electrodes were mounted to a plastic electrochemical cell with an exposed area of 0.28 cm². This geometric area is used to calculate the specific capacitance later. A Pt wire counter electrode and a Ag/AgCl reference electrode were used for all of the measurements. Electrolyte solutions of 0.1 M HCl, 0.1 M KCl, or 0.1 M NaOH were used. Cyclic Voltammetry and Chronoamperometry were carried out using an Autolab 302N Potentiostat and the three-electrode system.

A PANalytical Empyrean X-ray Diffractometer (XRD) with a PIXcel^{3D} detector was used to obtain XRD patterns of the as-grown thin films on single crystal and polycrystalline substrates. Wavelength dispersive x-ray fluorescence spectroscopy (WDXRF) and energy dispersive spectroscopy (EDS) were used to measure the composition of the films. A LEO 1530 VP Scanning Electron Microscope (SEM) is used to obtain the images of the surface morphology. Raman spectroscopy measurements are performed using 532 nm laser light at a power of 0.10 W on a Jobin Yvon U1000 spectrometer configured with a confocal microscope. The light was focused on the surface of CDC films to a size of approximately 0.30 mm diameter. The spectra demonstrated were the average of 8 scans at a binning level of 4. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) measurements were done with an Agilent 7500 ICP-MS equipped with an Ar ICP touch and a quadrupole mass analyzer. $V(NO_3)_2$ solutions in 5% HNO_3 were used as standards. Data was accumulated over 2 minutes at a sampling flow rate of 0.5 mL/min. Conductivity was obtained by a 4-point probe measurement with an even space of 0.635 mm between each two neighbor probes. A Keithley 224 current source and an HP 34401A multimeter were used to measure the four-terminal resistance using current reversal to account for thermal offsets.

Results and Discussion

Figure 1 presents the XRD results for the as-grown VC and V_2C films demonstrating the role of the C_2H_2 partial pressure on the phases grown since the only parameter changed between the depositions for the sample in the left panel, VC (grown with 2.0% mol/mol C_2H_2), and the right panel, V_2C (grown with 1.25% mol/mol C_2H_2). At a higher C_2H_2 molar fraction (2%), diffraction peaks of VC (111) and VC (002) planes of a cubic crystal structure can be observed clearly at about 37.3 and 43.4 degrees, respectively. Peaks around 41.6 degree come from the substrate, (001) planes of c-axis Al_2O_3 . While when the C_2H_2 molar fraction is lower (1.5%), the XRD pattern showed V_2C diffraction peak at about 39.5 degree which come from the (002) planes of a hexagonal V_2C crystal; meanwhile, the VC peaks are not observed. The substrate can be broken by scoring the backside and snapping using glass slides. The cross-section SEM images showed

that the carbide films' thickness has been adjusted between 2.0 and 2.6 μm by controlling the time of deposition. The crystal structures of the carbides do not depend on the thickness of the film. The as-grown carbide thin film have metallic conductivity, $3.3 \pm 0.1 \times 10^3 \text{ S}\cdot\text{cm}^{-1}$ for VC and $1.8 \pm 0.1 \times 10^3 \text{ S}\cdot\text{cm}^{-1}$ for V_2C , therefore, the films were used as electrodes for electrochemical measurement without other treatments.

Figure 2 shows the cyclic voltammograms (CV) on V_2C and VC electrodes, respectively, in a 0.1 M KCl electrolyte solution. It can be seen that oxidation occurred when the electrode potential was increased to or beyond 0.4 V for V_2C and 0.5 V for VC. The Faradaic current increased as the electrode potential is swept to be as high as 1.0 V. When the electrode potential was held lower than these critical values, no oxidation current was observed even after many scans. The pristine V_2C electrode is black color and the surface is shiny; after the oxidation the electrode is still black but not shiny, indicating the increase of surface roughness. In 0.1 M HCl, 0.1 M KCl, or 0.1 M NaOH electrolyte solutions, similar results were observed, with an ever-increasing cathodic current that showed up after the critical potentials. To determine the exact species that is produced by the electrochemical oxidation, further characterization of the solution is required, though the vanadium in solution can be detected immediately by ICP-MS after the oxidation current was observed. In acidic or

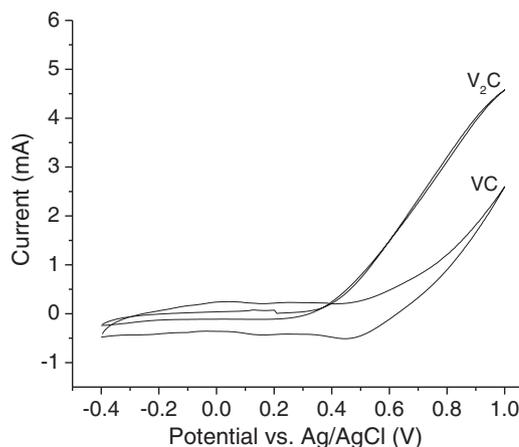


Figure 2. CV curves of V_2C and VC electrodes in 0.1 M KCl electrolyte solution at a scan rate of 0.1 V. s⁻¹.

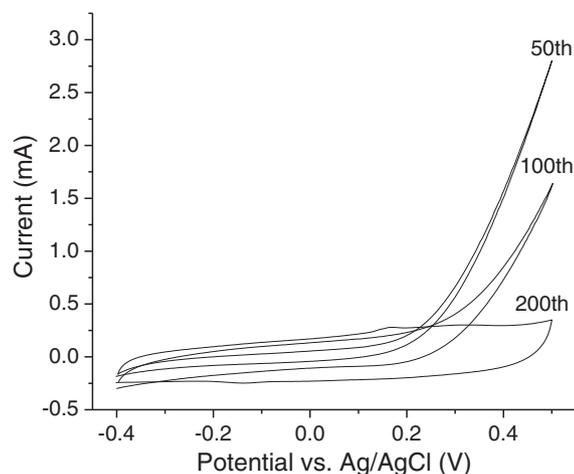
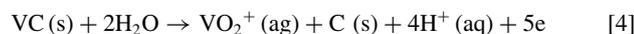
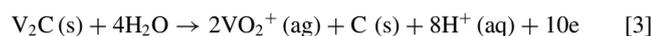
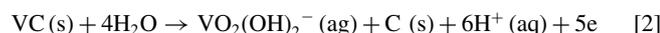
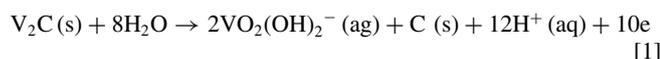


Figure 3. CV curves on V_2C in 0.1 M KCl at a scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$. The 50th, 100th, and 200th scans are shown.

neutral aqueous solutions, vanadium can be oxidized to be V(V) ions, such as VO_2^+ (in an acidic solution) or $VO_2(OH)_2^-$ (in a neutral solution), at a potential of 0.5 V vs. Ag/AgCl or higher.¹² Therefore, possible half reactions in 0.1 M KCl are shown in Equations 1–4. Since the detailed reaction mechanism is not the focus of this paper, a more detailed investigation of the electrode reaction mechanism will be pursued in the future.



The vanadium concentration increased gradually when more cyclic voltammetric scans were performed or when holding the applied potential above the critical potential for a longer period of time. Meanwhile, the CV curve also evolved as the number of scans increased. Figure 3 shows the 50th, 150th and 200th cycles of the CVs when a V_2C electrode was scanned in a 0.1 M KCl solution. It can be seen that vanadium was gradually stripped from the electrode surface. The Faradaic current induced with applied voltages between 0.3 V and 0.5 V decreased gradually due to the smaller amount of V available on or near the surface; while the double layer charge/discharge current slowly increased as evidenced by the higher currents in the baseline between -0.4 V and 0.3 V .

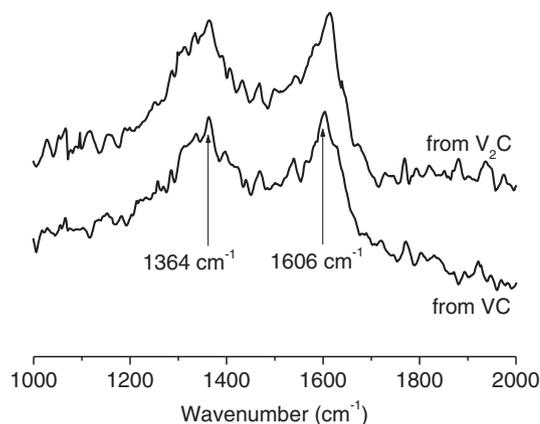


Figure 5. Raman Spectra of V_2C and VC substrates after electrochemical oxidation in 0.1 M HCl solution.

Nevertheless, after vanadium in the VC or V_2C was oxidized and dissolved in the solution, porous solid carbon (CDC) was left over on the electrode surface. Figure 4 depicts the surface morphology of the V_2C electrode before and after the electrochemical oxidation. After the electrochemical etching, the surface morphology of the electrode changed. The V_2C film has a surface microstructure consistent with columnar growth expected for the cubic carbide phase. The converted CDC film from the V_2C precursor demonstrates dramatic differences in microstructure, likely due to the fractional volume of the material removed. A series of pores at tens of nm size-scale can be observed in the SEM images. The pores, dark areas, recessed from the surface, have very clear boundaries with the carbon materials left over. It is expected that smaller nanopores ($<10 \text{ nm}$) are present but not observable in the SEM images. Figure 5 shows the Raman spectra of the V_2C and VC electrodes after electrochemical oxidation. Before electrochemical oxidation, no significant peaks were observed over the wavenumber range of $1000\text{--}2000 \text{ cm}^{-1}$ in the Raman spectrum. Scattering peaks at 1364 cm^{-1} and 1606 cm^{-1} showed up after the oxidation. These are typical peaks from the D-band (sp^3 hybridization) and the G-band (sp^2 hybridization) of carbon, indicating the formation of a CDC layer with atomic structure different from either diamond or graphite.⁸ It can also be seen that both peaks are relatively broad and the intensity of the two peaks are very close, which indicates that the electrochemically prepared CDC may have similar structure to CDC synthesized at $500\text{--}600^\circ\text{C}$ using the traditional chlorination method.² The fraction of vanadium removal and the surface morphology vary depending on the oxidation potential. When a 0.28 cm^2 V_2C electrode was tested, the maximum concentration of vanadium reached 9.3 ppm in 10 mL of electrolyte solution. Based on the density of V_2C ($5.665 \text{ g}\cdot\text{cm}^{-3}$),¹³ the total vanadium dissolved in the solution is equivalent to the vanadium in the top $0.66 \text{ }\mu\text{m}$ of the

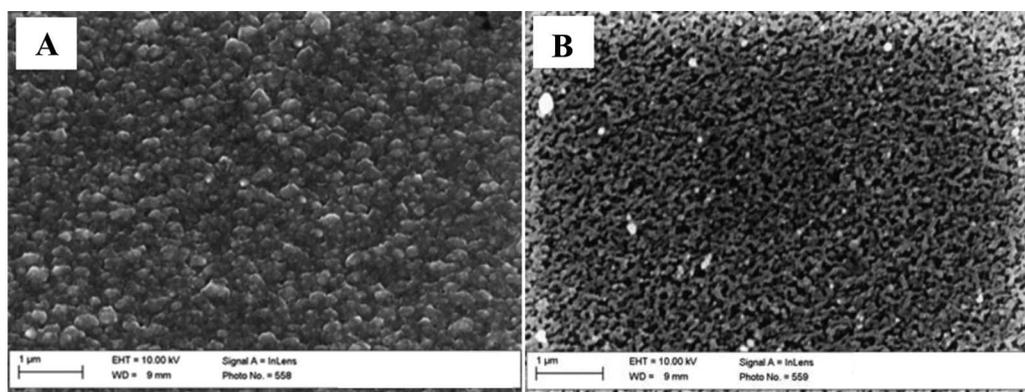


Figure 4. SEM images of V_2C thin film before (A) and after (B) electrochemical oxidation at 0.7 V.

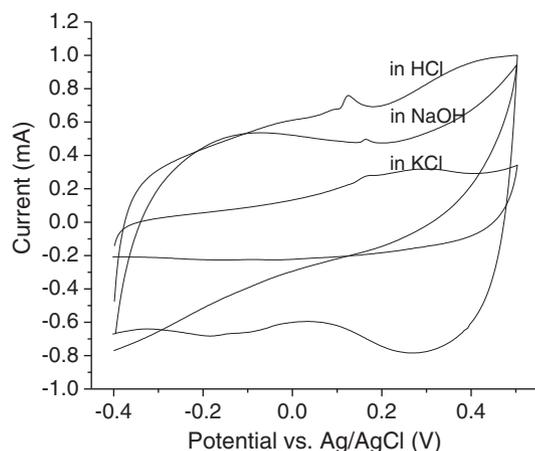


Figure 6. CVs of V_2C electrodes in 0.1 M KCl, 0.1 M HCl, and 0.1 M NaOH. The 200th cycles are shown. The scan rate was $0.1 \text{ V}\cdot\text{s}^{-1}$.

V_2C film. The factors that limits the electrochemical etching to the $0.66 \mu\text{m}$ close to the surface are not clear though a possible explanation is that when the CDC thickness approaches $0.66 \mu\text{m}$, both the electrolyte and the oxidized vanadium cations experience restricted transport through the network of pores limiting both oxidation and cation removal. When the potential is reversed, the vanadium cations redeposit.

The so-produced porous CDC on the surface of the substrate should have very large specific surface area and be excellent electrode materials for supercapacitors or other electrochemical applications. Figure 6 shows role of the electrolyte solution on the behavior of the CVs. An acidic solution, 0.1 M HCl, a basic solution, 0.1 M NaOH, and a neutral solution, 0.1 M KCl were used as electrolyte solutions for the electrochemical oxidation and test. The CVs were measured in the potential range between -0.4 V and 0.5 V . After the oxidation of the vanadium carbide reached its limitation, there was no more Faradaic current corresponding to the redox reactions. The current of the “bulgy” CV curve results from the charge/discharge of the double layer. The double layer capacitance (C_{dl}) can be estimated from either the area circled by the CV (electronic charge in coulomb) or the average current (I) of one segment of the cyclic scan and the scan rate (ν) ($C_{dl} = I/\nu$). The highest specific capacitance is observed in 0.1 M HCl solution, which is over the range of $\sim 90\text{--}100 \text{ F}\cdot\text{cm}^{-3}$. This value is estimated based on the fact that the exposed electrode area is 0.28 cm^2 and the V_2C layer is about $2.5 \mu\text{m}$. It is worth noting that only a fraction of the V_2C layer was etched, roughly a $0.66 \mu\text{m}$ depth in the previous case. If the upper limit of the capacitance were estimated based on this thickness, the specific capacitance should increase by a factor of nearly 3.8 ($\sim 2.5 \mu\text{m}$ vs. $0.66 \mu\text{m}$).

The electrochemical oxidation can be achieved by different electrochemical techniques, though the upper limit of vanadium removal and double layer capacitance are close. For example, a V_2C electrode was oxidized by controlled potential chronoamperometry in 0.1 M HCl solution with continuous stirring. An electrode potential of 0.6 V was applied initially and the potential increased stepwise by 0.05 V until a maximum of 0.85 V was reached, as shown in Figure 7A. The

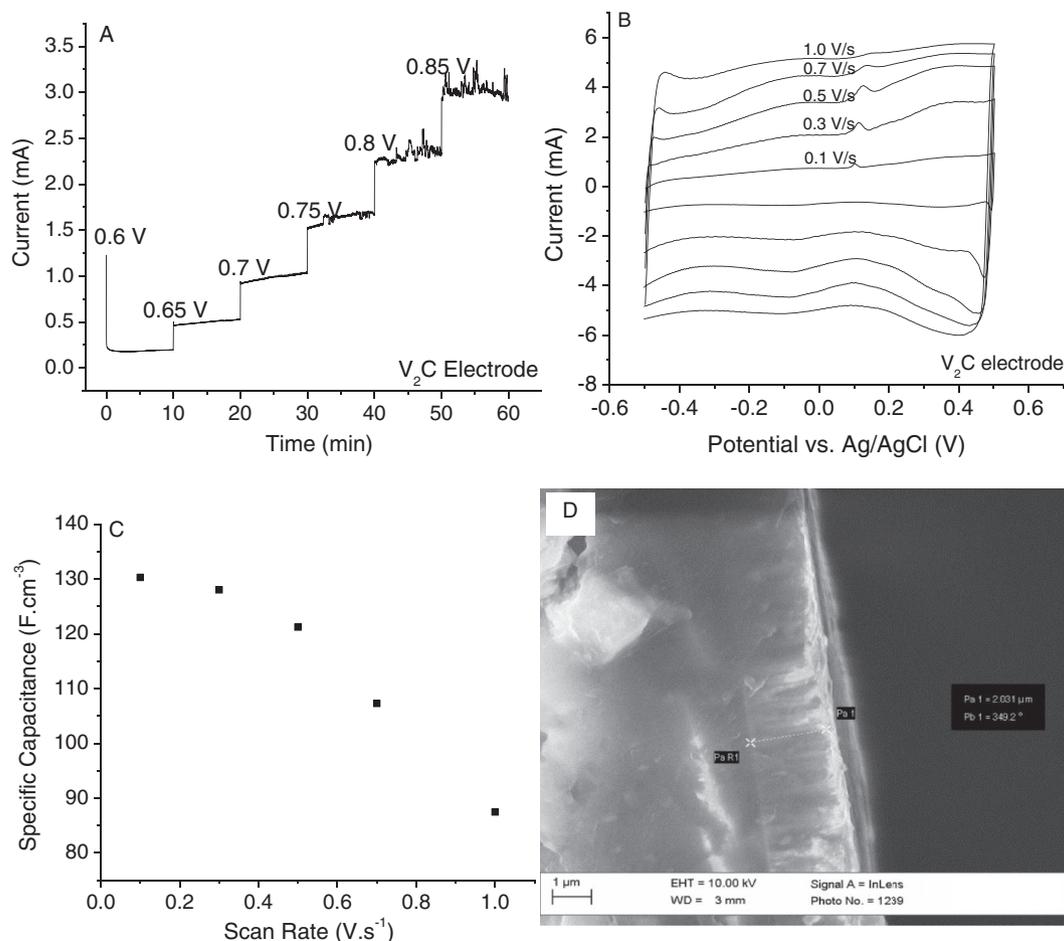


Figure 7. (A) Chronoamperometry of V_2C electrochemical etching at controlled potentials in 0.1 M HCl solution with constant stirring; (B) CVs of the etched electrode in 0.1 M HCl at various scan rates from $0.1 \text{ V}\cdot\text{s}^{-1}$ - $1.0 \text{ V}\cdot\text{s}^{-1}$; (C) specific capacitance vs. scan rate; (D) SEM image of the cross-section view of a V_2C thin film, thickness $2.03 \mu\text{m}$.

electrode potentials were held at their fixed values for 10 minutes each time. After the potential was applied, the current went to its limiting value quickly and then increased each time when the potential was stepped up. In each 10-min time range, the current increased slightly (except at 0.85 V), indicating the continued oxidation of vanadium. After the total one-hour treatment, the electrode changed from shiny black to flat black. The electrolyte solution was diluted to 10 mL by 5% HNO₃ and the vanadium concentration in the diluted solution is about 29 ppm, once again, it is equivalent to the total vanadium in approximately 0.72 μm (slightly deeper than that from the oxidation by cyclic voltammetry) of V₂C using the exposed area of about 0.8 cm². The electrode was then mounted onto an electrochemical cell with an exposed area of 0.28 cm². CVs in 0.1 M HCl over the potential range of -0.5 V ~ 0.5 V at various scan rates are shown in Figure 7B. Nearly rectangular-shaped CVs were observed, which is the characteristic of nearly "ideal" charge-discharge of a double layer capacitor. For an ideal capacitor, the charge/discharge current is proportional to the rate of the potential ramp. In Figure 7B, we also observed that the current increased with increasing scan rate, but the increase was not perfectly linear. This may be due to the partial charge at higher scan rates and a more complete charge at lower scan rates. This speculation agreed with the specific capacitance estimated at each of the scan rates as shown in Figure 7C. CV curves on the so-produced CDC electrode are nearly identical when tens of scans were tested. Long-term charge/discharge stability of the electrode has not been investigated. The specific capacitance values were calculated based on the total precursor thickness of 2.03 μm (Figure 7D), although only the top fraction of thin film is oxidized to be CDC. At a scan rate of 0.1 V/s, the CDC electrode has its highest specific capacitance of ~0.026 F/cm² or ~130 F/cm³; the specific capacitance reduced gradually to 0.018 F.cm⁻² or 87.5 F.cm⁻³ at a scan rate of 1.0 V.s⁻¹. Six V₂C films were electrochemically oxidized by the same method and all tested in 0.1 M HCl solution. The results demonstrate excellent reproducibility of 0.023 ± 0.003 F.cm⁻² at a scan rate of 0.1 V.s⁻¹.

Conclusions

Experimental results demonstrate that the vanadium carbides, V₂C and VC, grown as textured thin films on sapphire substrates can be

oxidized electrochemically at room temperature in acidic, basic, or neutral solutions. The critical electrode potentials are 0.4 V and 0.5 V vs. Ag/AgCl for V₂C and VC, respectively. The electrochemical oxidation partially removed the vanadium in the binary carbide leaving CDC of about 0.66–0.72 μm on the electrode surface. This is a new method of obtaining CDC in contrast to the usual etching using chlorination. The oxidation method has significant energy savings, is environmental friendly, and convenient in operation. It also allows for the conversion of a binary carbide to CDC on any substrate. The so-produced CDC has very large specific surface area and is a very promising material for thin-film supercapacitors. In 0.1 M HCl solution, the double layer capacitance of the CDC material is as high as 0.026 F/cm² or 130 F/cm³.

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