Synthesis of Carbide Derived Carbon by Electrolysis in Molten Chloride Salts

in Open Air

By

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THESIS

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ABBREVIATIONS

a-C: amorphous Carbon
a-C:H: amorphous Carbon with Hydrogen
CDC: Carbide Derived Carbon
CNTs: Carbon Nanotubes
DLC: Diamond-Like Carbon
DSC: Differential Scanning Calorimetry
FWHM: Full Width at Half Maximum
LO: Longitudinal Optic
NCG: Nanocrystalline Graphite
OM: Optical Microscopy
SEM: Scanning Electron Microscopy
SEM-EDS: Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy
SSA: Specific Surface Areas
STP: Standard Temperature and Pressure
ta-C: tetrahedral amorphous Carbon
TO: Transverse Optic
UV: Ultraviolet
XRD: X-ray diffraction

SUMMARY

Carbide-derived carbon (CDC) refers to a form of carbon produced from carbon containing substrates. The prepared carbon with the combination of diverse carbon phases in one material not only is good at tribology and gas storage but also can be used in capacitors due to its high surface area. Compared to previous CDC synthesis methods, an improvement producing CDC by electrolysis in LiCl-KCl in open air is proposed in this work which makes the process more convenient and low-cost. Produced CDC, both SiC-CDC and TiC-CDC, showed broader D and G peaks, larger ratio of intensity (I_D/I_G) and FWHM (full width at half maximum) than those of untreated SiC or pure graphite on Raman results, indicating that CDCs with more disordered structures which may contain nanocrystalline graphite (NCG) and amorphous carbon (a-C) are successfully produced. The theoretical thickness of sample 4 is estimated by calculation which is approximately 1.44 μ m.

1. INTRODUCTION

Carbide-derived carbon (CDC) refers to a form of carbon produced from carbon containing substrates. It not only is good at tribology and gas storage but also can be used in capacitors because of its high surface area. According to previous reports, CDC has been produced by etching carbide precursor with chlorine gas at temperatures above 900°C[1], laser heating of SiC[2], vacuum decomposition of SiC at temperatures above 1200°C[3]. Recently another method, reactive anode electrolysis in molten KCl-NaCl at a temperature range 700-800°C, has been proposed by Mika[4] to avoid health and environmental hazards when dealing with chlorine gas.

Following the prior work, making CDC in open air became attractive since it will make the process more convenient and easier to control, which cannot be accomplished if the electrolysis is done under a relatively high temperature since produced carbon will react with oxygen when the temperature is higher than $600^{\circ}C[5]$.

Therefore, the purpose of this work is to show that CDC can be produced on Ti-6Al-4V by electrolysis in molten melts in open air. LiCl-KCl molten melts was selected for its lower melting point than NaCl-KCl used in Mika's research[4], which makes it possible to do electrolysis in open air. Ti-6Al-4V, as a well-known biomaterial, is rarely considered as a candidate for hip implants bearing material because of its poor tribocorrosion behavior which is supposed to be improved by produced CDC films. Before electrolysis, carburization treatment needs to be done on Ti-6Al-4V to obtain a carbide precursor.

2. LITERATURE REVIEW

2.1 Carbide-Derived Carbon

Carbide-derived carbon (CDC) is the nanostructured carbon material derived by extraction of metal from a carbide precursor, which may have sp³- or sp²- bonded carbon phases.

Depending on the experimental condition such as time, temperature, substrate and voltage, several carbon structures were found in CDC before. For example, graphite, carbon nanotubes (CNTs), tetrahedral amorphous carbon (ta-C) and amorphous carbon(a-C), have been observed in SiC-CDC by S.Welz et al.[1]. CDC describes a process for forming carbon and can have properties of any of the different allotropes of carbon. For example, Welz et al.[6] synthesized nanocrystalline diamond by chlorination at 1000°C. After continued heat treating of nanodiamond, graphitic carbon containing carbon onions formed. They also reported that the presence of hydrogen is not the necessary condition to synthesize diamond, but it can stabilize the nanocrystal and therefore thicker diamond-structure layers formed. Moreover, another report[7] showed that both the carbide precursor and the operating temperature have influence on the structures of CDC. There is no clear correlation with the non-sp² structures formed but carbides with larger C-C distance promotes rearrangement which leads to a sp² rich graphite-like structure whereas shorter C-C distance result in CDC with lower sp² content. The property of CDCs being able to form diverse structures makes it an ideal material for applications in gas and electrochemical energy storage[8] or any other applications where pore size and distribution are dominant.

2.2 Synthesis of carbide-derived carbon

2.2.1 Synthesis of Carbide Derived Carbon by Etching in Gaseous Chlorine

CDC can be produced from several chemical and physical synthesis methods. The first synthesis of CDC recorded was reported by Y.G.Gogotsi et al.[9] in 1997 by etching materials in chlorine gas. The most common chemical synthesis method is chlorine treatment of metal carbide in the presence of chlorine (or other halogen) gas at moderate to high temperature. In the process, chlorine reacts with the metal to form a volatile compound and leaving carbon behind. Examples are listed below for SiC from equation 2.1 and 2.2. The formation of CCl₄ in equation 2.1 is always slower than the formation of CDC. This ensures the existence of CDC structure along with the consumption of other products such as Si.

$$SiC(s) + 2Cl_2(g) \rightarrow CCl_4(g) + Si(s) (2.1)$$
$$SiC(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + C(s) (2.2)$$

The chlorination temperature for producing CDC is reported at the range from 200°C to 1200°C for different carbides. Since graphite is the most thermodynamically stable form of carbon at high temperatures, it results in the higher the temperature of chlorination, the more CDC is observed to exist in graphitized form. It has been reported that since most of the reported CDC preparations have a chlorination temperature in excess of 1000°C, this leads to graphite becoming the main structural form of CDC, thus causing most CDC materials to shrink during the conversion process.

2.2.2 Synthesis of Carbide Derived Carbon by Electrochemical Etching in Aqueous Solutions

In addition of those high temperature application described above, Lukatskaya et al.[10] developed a method for synthesizing CDC by electrochemically etching three MAX phases in an aqueous solution with NaCl and HCl or HF at room temperature. As an example, the reaction of electrochemically etching Ti₂AlC is shown by Equation 2.3. The term of MAX phases is from their general formula which is $M_{n+1}AX_n$ (n=1,2,3), where M stands for transition metals, A mainly means IIIA or IVA elements, and X is the representative of either carbon or/and nitrogen.

$$Ti2AlC(s) + 3 HCl(aq) + 4 H_2O(l) \rightarrow C + 2TiO_2 + H_2(g) + AlCl_3(aq)$$
 (2.3)

2.2.3 Synthesis of Carbide Derived Carbon by Reactive Anode Electrolysis in Molten Salts As discussed above, the electrical conductivity of MAX phase carbides in Lukatskaya's work[10] such as Ti2AlC, Ti3AlC2 and TiSiC2 are sufficient to support electrochemical processes even in room temperature. However, unlike metals, carbides such as SiC may still not have enough conductivity except under high temperature. With these, Mika[4] proposed that electrochemical processes that use molten salts instead of aqueous solutions may become more suitable for this application. As a result, Ti2AlC-CDC and SiC-CDC composed of an amorphous carbon matrix that contains nanocrystalline graphite and graphite were successfully produced by electrolysis of SiC, TiC and MAX phase Ti2AlC in molten salts under Argon atmosphere, shown in equations through 2.4 to 2.6.

$$\begin{aligned} \operatorname{SiC}(s) + 4 \operatorname{NaCl}(l) &\to \operatorname{SiCl}_4(g) + \operatorname{C}(s) + 4 \operatorname{Na}(l) \ (2.4) \\ &\operatorname{TiC}(s) + 4 \operatorname{NaCl}(l) \to \operatorname{TiCl}_4(g) + \operatorname{C}(s) + 4 \operatorname{Na}(l) \ (2.5) \end{aligned}$$
$$\begin{aligned} \operatorname{Ti2AlC}(s) + 11 \operatorname{NaCl}(l) \to \operatorname{TiCl}_4(g) + \operatorname{AlCl}_3(g) + \operatorname{C}(s) + 11 \operatorname{Na}(l) \ (2.6) \end{aligned}$$

Other than the methods mentioned above, CDC can also be prepared by laser heating of SiC[2] and vacuum decomposition by extracting metal atoms in the carbide at a high temperature of 1200°C or more in a vacuum environment[11]. Compared to the previous methods, this process takes advantage of the high melting point and boiling point of carbon, which melts and evaporates metals in carbides under high temperature and leaving only carbon behind. It has been reported

that the CDC produced by this method has higher order of graphitization and thus can produce carbon nanotubes and graphene[12].

2.3 Applications of CDC

As mentioned before, CDC is the carbon layer grown from carbon precursor such as SiC, TiC and some MAX phases, the structure of prepared CDC depends on the experiment conditions. The produced carbon layer contains amorphous carbon and onion type carbon and may also have graphite and nanocrystalline diamond. The prepared carbon combining such diverse carbon phases in one material has applications in supercapacitors, biomaterials, and tribology.

2.3.1 Supercapacitors

Generally, supercapacitor electrodes are composed of mixtures of activated carbon with polymeric binder and conductive additives. High specific surface area and good electrical conductivity are normally two main factors to choose activated carbon[13]. It was reported that CDC with tunable porosity and conductivity had a higher gravimetric and volumetric capacitance compared to activated carbons, [14]. Dash[15] et al. prepared CDC by thermo-chemical etching of TiC in chlorine gas, results showed that the structure of this TiC-CDC is highly disordered in the temperature range 200-1200°C. Low synthesis temperature resulted in small pores with a narrow size distribution, large pores formed when the temperature is above 800 °C. CDC synthesized in the temperature range 600–800°C show great potential for energy-related applications. As reported by Gao et al[14], they produced TiC-CDC by chlorination in a temperature range 200-1000°C, the CDC produced at 1000 °C shows best performance, the capacitance reached 135 F/g in aqueous and 120 F/g in organic electrolytes. Zhao et al.[16] prepared TiC-CDC by chlorination. The synthesized carbon has a large surface area which is above 100 m²/g. The highest specific surface area and the highest specific capacitance were obtained at operating temperature of 400°C. The specific capacitance increased with increasing the amount of microporous area.

2.3.2 Gas Storage

The storage of gases in a solid sorbent is remarkably important for their capturing, so as to prevent environmental harm (e.g., CO₂, SO₂), for storing the gas for later use as an energy source (e.g., H₂) or medical applications (e.g., NO).[17] CDC has the Brunauer–Emmett–Teller (BET) surface areas which are larger than 2000 m²/g. Also, it contains a large volume of micropores. The porous structures of CDC make them the promising candidates for the storage of hydrogen and other gases.

2.3.3 Lithium-ion Batteries

Significant research have been carried out on searching for candidate anodes materials for Li-ion batteries due to their increasingly popularity. CDC was used as lithium-ion anode materials in Kotina's report[18], they studied the diffusion behavior and mechanism of lithium ions in SiC, TiC and Mo₂C-CDC. As a result, the obtained diffusion coefficients vary from 10⁻⁹ to 10⁻⁷ cm²/s which depends on the different pore size. TiC-CDC was also studied as anode materials by Sakamoto et al. at 600°C, 1000°C, and 1200°C. Due to large specific surface areas (SSA) of the samples, high irreversible capacities were obtained from the first cycling. CDC synthesized at 600°C by chlorination showed the most disordered structure and the highest specific capacity which is around 290 mAh/g.[19] These reports[18]–[20] indicate that CDC is a promising candidate material for lithium-ion batteries electrodes and more studies on pore size and particle size control are still needed.

2.3.4 Tribological Applications

As reported by A. Erdemir et al[21], the friction coefficient of prepared CDC in open air is close to that of graphite and is generally through 0.15 to 0.25. However, the friction coefficients of CDC tend to decrease with decreasing humidity and increasing loads. Whereas, increasing sliding velocity does not affect its frictional behavior significantly. McNallan et al.[22] synthesized SiC-CDC which shows smaller friction coefficient than untreated SiC and they pointed out that the tribological properties of CDC may be related to the nanoscale structure of carbon, which includes nanoscale diamond, carbon onion and nanoporous amorphous carbon. After further treating CDC in high temperature which can decrease the content of residual chlorine in the structure, the friction coefficient was found further reduced. Another research[23] on the effect of reaction temperature on the tribological behavior of CDC was carried out by Bae et al, the results show that the extent of carbon formation can be controlled by changing the operating temperature and chlorine gas mixture. The frictional coefficient decreases, and the wear rate increases until reaching a certain temperature, beyond which the wear rate decreased.

2.3.5 Biomaterials

CDC has been reported to have good mechanical properties and tribological properties depending on the different synthesis conditions.[22], [24], [25] Lau[26] proposed that CDC prepared by chlorination at high temperatures was considered to potentially be a novel biomaterial for hip implants because of its excellent tribological properties in non-biological systems, she found that Biocompatible CDC films can be produced by changing chlorination conditions and a further postchlorination hydrogen treatment.

2.4 Carburization of Ti-6Al-4V

Ti-6Al-4V is one of the most common used titanium alloys which are applied in a wide range such as biomedical, aerospace and chemical industries due to their high specific strength, good corrosion resistance which is attributed to the compact and passive oxide film on the surface, and excellent biocompatibility[27], [28]. However, a main restriction of these titanium alloys is their poor tribological behavior, when these alloys are used to make implants in a living body, mechanical wear will gradually remove the passive surface material [27], the corresponding wear and released metal ion can aggravate corrosion reaction[29]. In order to improve their tribological properties, several different surface modification techniques such as physical vapor deposition[30], [31], plasma and laser nitriding[31]–[33], thermal oxidation[34], [35], ion implantation[36], were applied to titanium alloys, mainly to the more widely used Ti-6Al-4V.

In order to make CDC on the surface of Ti-6Al-4V to improve their tribocorrosion behavior, carburization process is necessary to obtain a carbide precursor. According to different medium, there are three general methods which are gas, liquid and solid carburization. Gas carburization process was reported by Luo et al.[37][38], C₂H₂ gas was used as carbon source make titanium cermet on the surface of Ti-6Al-4V under high temperature and vacuum to improve their mechanical and corrosion properties. Liao et al.[39] carburized TiAl alloy by gas-metal reaction as a result of showing better corrosion resistance than the untreated sample. As reported by Cheng et al.[29], after 48-hour solid carburization treatment on Ti-6Al-4V, improved resistance to erosion and tribocorrosion have been shown to have few drawbacks, produced patchy oxycarbide reduced corrosion resistance.

In this work, similar solid carburization process as described in Cheng's work[29] was used to modify Ti-6Al-4V surface to obtain a carbide precursor from which CDC can be made. Although this methodology may result of the sacrifice of corrosion resistance, considered our goal to synthesize CDC from carbide precursor and more equipment are needed to do gas carburization which is required to be done under vacuum to avoid oxidizing Ti alloys and diluting source gas, it is still a low cost and effective choice to get Ti-6Al-4V carburized.

2.5 Molten Salts

Molten salts are salts which are solid at standard temperature and pressure (STP) but enters the liquid phase due to elevated temperature. Molten salts melts are commonly used as baths where electrolysis is done to prepare metals, which is different from our goal focus on formation of CDC.

2.5.1 Previous work on molten salts

A few studies have been reported on the synthesis of alloys by electrolysis in molten salt by a few research groups. Ueda et al. have prepared a resistive coating of Al alloy layers on the substrate by electrolysis from molten salts[40], [41]. Electrolysis was applied in a low-temperature molten salt for the formation of the coating. This resulted in a uniform and thin coating on the substrate which had low production costs. Several studies were conducted and reported on the formation of alloy electrodeposits of Al–Ni, Al–Cr, Al–Ti, Al–Mn and Al–Pt from low-temperature molten salts[41]–[44]. GH Ağaoğlu et al[45]. produced Mg-Ni alloys by molten salt electrolysis and diffusion method in KCI-NaCl based melts. Smolinski et al.[46], [47] studied the production method of Mg–Li by electrolysis in molten salt in a temperature range of 500–630°C. Zeng et al.[48] performed experiments to prepare Mg–Li alloys by electrolysis in LiCl-KCl in a lower temperature range of 420–510°C and to investigate the electrochemical behavior of Li by transient

electrochemical techniques, such as cyclic voltammetry, chronoamperometry and chronopotentiometry. Zhang et al.[49] prepared Mg-Li-La alloys in a molten LiCl-KCl-KF-MgCl₂ containing La₂O₃ at 943K by using an electrochemical method. The electrolytic bath was prepared by LiCl-KCl melts in an alumina crucible, the chlorides were dehydrated at 873K and 573K to remove residual water before experiment, respectively. The products were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical microscopy (OM) and the results showed that preparation of this alloy by electrolysis is feasible. In another work, Wang et al.[50] studied electrochemical behavior of Cerium ion in molten LiCl-KCl in the temperature range of 673-783K and graphite crucible was used to contain the molten salts. Cyclic voltammetry was done on the sample, and therefore, diffusion coefficient was obtained.

To sum up, several kinds of alloys were obtained by molten salts electrolysis in these reports. Our experimental setups share some basic features in common with theirs since the main reaction of electrolysis process are similar. However, the objectives of these works are achieving alloys or a certain metal (cathode products) through the process, which is different from our attention on the formation of carbon (anode products).

2.5.2 Selection of molten salts

From previous work, Mika has synthesized SiC-CDC at 700°C and 3V in NaCl-KCl molten salts[4]. In this work we firstly treated SiC in pure NaCl melts at 825°C and 3V for 30 mins, shown in equation 2.4, reactor was kept air tight under a positive pressure of argon or otherwise reaction products will burn in infiltrated air. In aforementioned reports, several researches were done in LiCl-KCl melts. From the phase diagram shown in figure 2.1[51], when mole fraction is 0.592, the melting point of LiCl-KCl is 353°C, which is much lower than that of NaCl-KCl or pure NaCl.

In addition to some advantages of low operate temperature such as energy saving and longer life for experiment equipment, the main reason why the low temperature is attractive to this research is it made it possible to do the experiment in open air because pure graphite starts to react with oxygen above 600° C, as shown in figure 2.2[5], at a burn-off temperature of 800° C all the graphite is oxidized to CO or CO₂ gas. Therefore, LiCl-KCl was used as baths for following runs, as shown in equation 2.7. According to Mika's calculation[4], at 353° C, LiCl is the dominant species in molten salts.

$$4\text{LiCl} + \text{TiC} = \text{TiCl}_4 + \text{C} + 4\text{Li} (2.7)$$



Figure 2.1. Phase diagram of KCl-LiCl molten salts[51].



Figure 2.2 Thermogravimetric analysis with pure graphite powder in air, heating rate 5 K/min[5].

2.6 Characterization techniques

Raman spectroscopy is a vibrational spectroscopic technique used to measure intensity of inelastically scattered light from molecules. To determine whether the vibration is Raman active or not, the selection rule must be applied to each normal vibration. From classical approach, when putting a molecule in an electrical field E (laser beam), an electrical dipole moment p is produced. The relation between them can be expressed as:

$$\mathbf{p} = \mathbf{\alpha} \cdot \mathbf{E} \quad (2.8)$$

Here, α is polarizability which is a constant. According to quantum mechanics, if the polarizability changed during the process, the vibration is Raman-active. However, in actual situation, the simple relationship as shown in Equation 2.8 cannot describe a normal vibration which happens in three dimensions. Equation 2.8 therefore can be written in a matrix form:

$$\begin{split} P_x &= \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \\ P_y &= \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \\ P_z &= \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \end{split}$$

Due to normal Raman effect,

$$\alpha_{xy} = \alpha_{yx}, \ \alpha_{xz} = \alpha_{zx}, \ \alpha_{zy} = \alpha_{yz}$$

the matrix then can be reduced as

$$\alpha_{xx}x^2 + \alpha_{yy}x^2 + \alpha_{zz}z^2 + 2\alpha_{xy}xy + 2\alpha_{yz}yz + 2\alpha_{zx}zx = 1$$
 (2.9)

To make the polarizability visualized, Wong[52] wrote Equation 2.10 as

$$\frac{x^2}{\left(\frac{1}{\sqrt{\alpha_{XX}}}\right)^2} + \frac{y^2}{\left(\frac{1}{\sqrt{\alpha_{YY}}}\right)^2} + \frac{z^2}{\left(\frac{1}{\sqrt{\alpha_{ZZ}}}\right)^2} = 1 \qquad (2.10)$$

and plot $1/\sqrt{\alpha}$ to form a polarizability ellipsoid. An example can be seen in Figure 2.3. which shows changes in polarizability ellipsoid of CO₂, if size, shape or orientation of the ellipsoid, any of them changes during the normal vibration, the vibration is Raman-active.



Figure 2.3. changes in polarizability ellipsoid during vibration of CO2 molecule[53]

Based on selection rules and previous reports, Raman spectroscopy can be used to identify carbon films. The diverse physical properties of carbon films depend on the ratio of sp² to sp³ bonds [54].

A ternary phase diagram of amorphous carbon is shown in figure 2.4[55]. In general, any combination of sp^3 , sp^2 and even sp^1 sites can be found in an amorphous carbon, with the possibility of hydrogen and nitrogen being present.



Figure 2.4 Ternary phase diagram of amorphous carbons. [56]

Diamond-like carbon (DLC) is an amorphous carbon (a-C) or amorphous carbon with hydrogen (a-C:H) with a significant fraction of sp³ bonds, it has high mechanical hardness, chemical inertness and optical transparency. As can be seen in the phase diagram, tetrahedral amorphous carbon (ta-C) and the hydrogenated analogue ta-C:H are the DLCs with a high sp³ content of 80–90% and a-C:H often has a low C–C sp³ content.

In Raman spectra for the structures with sp² bonding, the G and D peaks can be found for in the 800 - 2000 cm⁻¹ region, which lie at 1560 and 1360 cm⁻¹, respectively. The presence of D band is due to the breathing modes of rings, G peak is because of the stretching mode of all sp² bonding in both chains and rings, as depicted in figure 2.5. Thus, no rings, no D peak[56]–[60]. Figure 2.6

shows Raman results of Fe₃C-CDC, for graphite structure without defects, there is only an intense G band on Raman spectra, since the breathing mode of rings is inhibited by the densely packed hexagonal carbon structure.



Figure 2.5 Illustration of breathing mode (left) and stretching mode (right)



Figure 2.6 Raman spectra of carbon produced by chlorination of Fe3C for 3 h at different temperatures. [61]

Also, there is a T peak can be observed at 1060 cm⁻¹ which is due to the C-C sp³ vibrations, seen only in ultraviolet (UV) excitation[55], [62], [63]. Therefore, it can be concluded that depending on the intensity ratio of D and G peaks (I_D/I_G), the location and width (also known as full width at half maximum FWHM) of the peaks, we can roughly identify structures of produced carbon materials.



Figure 2.7: Three-stage model of variation of the Raman G position and the D-to-G intensity ratio, I(D)/I(G), with increasing disorder[53]

As shown in figure 2.7, Ferrari and Robertson[56] used a three-stage model to explain the Raman spectra of all carbon films:

In the first stage, from graphite to nanocrystalline graphite (nc-G), the in-plane crystalline size within an ordered graphite layer becomes smaller, G peak position moves from 1581 cm⁻¹ to 1600 cm⁻¹, I(D)/I(G) increases from 0 to 2.

In the second stage, from nc-G to sp^2 a-C, even though sp^2 is still the main bonding in the structure, there are topological disordering introduced into the graphite layer, the position of G peak moves to 1510 cm⁻¹ since the vibrational modes was softened by the weaker bonds[54].

The last stage corresponds to the transformation of sp² sites to sp³ sites, from a-C to ta-C, the structure completely changes from ring to chain configurations. The G peak position increases to 1570 cm⁻¹, due to the confinement of π electrons in shorter chains[56]. I(D)/I(G) = 0 due to the absence of rings.

Also, the sp² configuration directly affects Raman spectra. In general, sp² configuration changes with the quantity of sp2 consistently, whereas in some cases, the sp² configuration varies independently from the sp² fraction, which is called non-uniqueness phenomenon, the Raman spectra will be therefore affected which is marked by the dotted arrows in figure 2.7(b).

Moreover, in this work, along with Raman spectroscopy, the actual melting point of molten salts were tested by differential scanning calorimetry (DSC). X-ray diffraction (XRD) was utilized on carburized Ti6Al4V to verify TiC layer was prepared on the surface of the alloy. Scanning electron

microscopy and Energy-dispersive X-ray spectroscopy (SEM-EDS) was also adopted to analyze types and quantity of elements in products.

3. EXPERIMENT METHODS

3.1 Experiment setup

For experiments with SiC (from SiC heating elements) and several runs with carburized Ti-6Al-4V substrates, a quartz tube was used as the reactor. Since carbon burns at a relatively low temperature when exposed to air, all the experiments with quartz tube were done under Ar gas to avoid loss of product. The reactor configuration is shown in figure 3.1. However, LiCl is too aggressive to the quartz tube, so a graphite crucible was then used as the reactor. Due to the relatively low melting point of LiCl-KCl molten salts which is 353°C, we tried several runs in open air, the reactor was assembled as shown in figure 3.2.



Figure 3.1: reactor configuration with quartz tube.



Figure 3.2: Reactor configuration with graphite crucible.

The TiC sample is attached to the electrode as shown in Figure 3.3(b). Drilled holes in the top and bottom of the coupon. The electrode was attached to the top hole and the sample was fixed to the argon lance using a nichrome wire at the bottom hole to prevent it from moving too much under agitation. No reaction of the bottom wire with the electrolyte was observed. The SiC substrate is fixed by cutting notches that retain wire as shown in Figure 3.3(a).



Figure 3.3: Fixturing of the SiC and TiC substrates before treatments. (a) SiC sample configuration (b) TiC sample configuration in inert gas (c) TiC sample configuration in open air

3.2 Experiment methods

- 3.2.1 Experiments with SiC sample
- a. Salts preparation

To remove moisture in the salts, pure NaCl was firstly dried at 400°C for 1h, after which the temperature was increased to 825°C, the transparent melted salts were observed after about 15mins. Then push the Ar gas input in the melted NaCl to get rid of the O₂ or H₂O trapped in the salts through bubbling. The system was cooled down to room temperature.

b. Electrolysis

The anode was assembled as shown in Fig.3.3(a). Heat up to 825°C, held the temperature for 15mins after reaching the temperature and connected the electrodes with power source. Turned on

power source and set to 3Volts. Slowly immersed the SiC sample into the salts for 10mins and turned off the power source. Removed the sample from salts before cooling down the system to room temperature.

c. Characterization

Each sample was characterized by a Renishsaw InVia Raman spectrometer. 532 nm green laser with the 50X objective was used to measure all spectra.

- 3.2.2 Experiments with TiC sample
- a. Carburization of Ti6Al4V

Grinded the samples to remove the oxidation film on the surface of Ti6Al4V, completely buried two samples in the graphite powder parallelly and made it compact by putting on an alumina tube as a load, shown in Fig 3.4(a)(b)(c)(d). Put the setup in a sealed horizontal quartz tube in the furnace as in Fig 3.5 and started to purge Ar gas for one hour to remove air before increasing temperature to 1000° C, under which the samples were treated for 24 hours. After cooling down to room temperature, all samples were ultrasonically cleaned in DI water for 15mins.







Figure 3.5. Carburization reactor configuration

b. Chlorination

Ar gas was induced for an hour to remove the air in the horizontal quartz tube, then the temperature was increased to 671°C. The carburized sample was treated under chlorine gas for 5mins and the temperature was kept for another hour.

c. Salts preparation

29.4g LiCl and 35.6g KCl were mixed and added into a Ni crucible. The salts mixture was then dried for 24h at 200°C. To identify the actual melting point, 9.11mg salts mixture was used for

differential scanning calorimetry (DSC) test. The temperature was set to 400°C, salts were melted and well mixed when it became transparent liquid.

For runs with quartz tube, Ar gas was purged in the salts for an hour to remove the oxygen or moisture trapped in the salts. Subsequent experiments using the same electrolyte only required one hour of drying at 300°C before starting the experiment since the powders had been solidified into a dense solid.

d. Electrolysis

Prior to electrolysis, the anode was assembled as shown in Fig.3.3(b). The voltage was set to 3Volts, then the carburized sample was slowly immersed in the bath for a certain time.

e. Characterization

DSC was used to obtain the actual melting point of KCl-LiCl mixture with a mole fraction of 0.592. Raman spectrometer was also performed on all samples in this part. Before each treatment, the carburized Ti6Al4V was verified by XRD for the presence of the TiC phase. Besides, the last sample in this part was inspected by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS), which can characterize morphology and distribution of CDC. Six runs were treated in this work, experiment conditions are summarized in table 3.1.

rable 3.1 Summarized experiment conditions for 0 runs							
Sample #	Sample 1	Reference results	Blank comparison	Sample 2	Sample 3	Sample 4	
Substrate Material	SiC	Carburized Ti6Al4V	Carburized Ti6Al4V	Carburized Ti6Al4V	Carburized Ti6Al4V	Carburized Ti6Al4V	
T (°C)	825	/	400	400	400	400	
Voltage (V)	3	/	/	3	3	3	
Time (Mins)	30	/	10	10	10	1	
Atmosphere	Ar gas	/	Ar gas	Ar gas	open air	open air	
Salts bath	Pure NaCl	/	LiCl-KCl	LiCl-KCl	LiCl-KCl	LiCl-KCl	

Table 3.1 Summarized experiment conditions for 6 runs

4. RESULTS AND DISCUSSION

4.1 Differential Scanning Calorimetry (DSC) results of KCI-LiCl eutectic mixture

Figure 4.1 shows DSC curves of KCl-LiCl eutectic mixtures with mole fraction of 0.592. Three endothermic peaks at approximately 92.76°C, 170.14°C and 353.26°C can be seen on the graph, corresponding to evaporation of water, decomposition of LiCl hydrate[64] and melting of KCl-LiCl salts [52], respectively. The actual melting point of salt mixture we used in experiments is consistent with the theoretical number on the phase diagram, which helps us to confirm that the salts were well mixed and completely melted at 400°C. Also, according to the peak at 170.14°C, we decided to dry the salts at 200°C to remove the moisture entirely.



Figure 4.1 DSC curves of molten LiCl-KCl salts

4.2 Characterization of Untreated SiC Substrate

Figure 4.2 shows Raman results of untreated SiC sample, a sharp peak at 965 cm⁻¹ is observed which corresponds to longitudinal optic (LO) bands of SiC. Deconvolution is not done on this Raman results since there is no obvious D and G bands.



Figure 4.2: untreated SiC: (a) Photograph of sample (SiC heating element) and (b) Intensity vs. Raman Shift signal. The cross and arrow on (a) show where we got Raman Spectroscopy (b)

4.3 Characterization of SiC Treated in NaCl at 825°C and 3V for 30mins under Ar atmosphere by Raman Spectroscopy (Sample 1)

Figure 4.3(a) shows the picture of SiC sample after treatment. Three obvious peaks can be seen on the Raman results, the sharp intense peak at 789cm⁻¹ corresponds to the transverse optic (TO) band of SiC. Compared to Raman spectra of untreated SiC, the peak located at 965cm⁻¹ almost disappear. As described by S. Nakashima et al.[65], defects in SiC structures affect their Raman results, especially the intensities of LO and TO bands. For instance, when they characterized SiC samples containing dislocations, stacking faults and antiphase boundaries at around the border of SiC and Si on (001) plane by Raman spectroscopy, the intensity of TO peak is much lower or weaker than that of LO peak. In this work, since we use SiC heating elements as our samples, it is uncertain that what exactly the defects are having influence on our Raman results, but it will not impact this study since the emergence of D and G band at 1353 and 1589 cm⁻¹ indicates that CDC was obtained through this process.

100% Lorentzian peak fitting was done by OriginLab[66] and R² is 0.972, fitting results are summarized in Table 4.1. FWHM is 146 cm⁻¹, ID/IG calculated is around 1.16 which means the synthesized CDC has a nanocrystalline graphite structure as described in Section 2.6.

Another thing needs to be pointed out here is, due to the low conductivity of SiC, the current during 30-minute electrolysis is low which is about 0.04 amps. In the subsequent experiments, we used carburized Ti6Al4V which has a higher electrical conductivity as our samples.





Figure 4.3: SiC treated at 825°C for 30 minutes at 3V: (a) Photograph of sample and (b) Intensity vs. Raman Shift signal with deconvolution results. The cross and arrow on (a) show where we got Raman Spectroscopy (b)

Center Grvty (cm ⁻¹)	Peak Type	FWHM (cm ⁻¹)	Max Height (a.u.)	Peak Area
789.026	Lorentz	7.630	6429.356	76348.206
1352.831	Lorentz	146.423	3442.723	735276.974
1589.199	Lorentz	92.645	2965.427	409037.636

Table 4.1: Fitting results for SiC treated at 825°C and 3V for 30 minutes.

4.4 Characterization of Ti6Al4V Substrate after Carburization by Raman Spectroscopy and XRD (Reference results)

Figure 4.4(a) shows pictures of two sides of cleaned carburized Ti6Al4V. Two Raman patterns were observed. No obvious peak shows in the figure 4.4(b) because TiC is not Raman active. In figure 4.4(c), three sharp peaks were observed which are D band at 1345cm⁻¹, G band at 1578 cm⁻¹ and the peak at 2698 cm⁻¹ which is a 2D peak, I_D/I_G was estimated to be 0.39, deconvolution results are summarized in table 4.2, the position and width of the two peaks is consistent with graphite. The reason why graphite can be detected on this sample is that graphite powder stuck in the surface of the material during carburization process cannot be completely removed. These Raman results are used as reference results.

XRD results of carburized Ti6Al4V are shown in Figure 4.5, the presence of three peaks at 36.1°, 42.1°C and 60.8°C shows the complex of titanium carbide (TiC) and Titanium monoxide (TiO). Based on the report[67], depending on the amount of oxygen in the structure, the oxygen impurity can lead to the pure TiC XRD peaks shifting from standard values which are 35.9°, 41.7° and 60.4°[68].Graphite was also observed in XRD which is consistent with Raman results.







Figure 4.4: Carburized Ti6Al4V: (a) Photographs of sample and (b) (c) Intensity vs. Raman Shift signal with deconvolution results. On (a) left, the cross and arrow show where we got Raman results (c); on (a) right, the cross and arrow show where we got Raman results (b).

Center Grvty (cm ⁻¹)	Peak Type	FWHM (cm ⁻¹)	Max Height (a.u.)	Peak Area
1344.800	Lorentz	42.521	1799.737	121259.146
1578.137	Lorentz	24.958	4657.148	181312.263
2698.402	Lorentz	65.277	2835.253	283183.271
2454.156	Lorentz	39.492	167.558	10269.518
2936.577	Lorentz	34.991	132.685	7120.197

Table 4.2: Fitting results for carburized Ti6Al4V



Figure 4.5: XRD results of Carburized Ti6Al4V

4.5 Characterization of TiC Treated in LiCl-KCl at 400°C for 10mins without Applying Voltage in Ar Gas by Raman Spectroscopy (Blank Comparison)

In this run, we immersed the carburized Ti6Al4V coupon in the LiCl-KCl melts for 10 mins without applying any voltage to verify that CDC is made through electrolysis process instead of direct reaction with the salt.

100% Lorentzian deconvolution is done on the Raman spectra which revealed D band at 1396 cm⁻¹, G band at 1581 cm⁻¹ and a 2D peak at 2711 cm⁻¹ which corresponds to a graphite structure. It is can be obtained visibly but also from area and FWHM of the peaks that D peak is relatively broad whereas G peak is sharp and intense, estimated I_D/I_G is 0.10, indicating that the structure is highly

ordered. Similar to reference results, this Raman pattern corresponds to graphite powder stuck in the surface. This Raman result is used as our blank comparison.



Figure 4.6: TiC Treated in LiCl-KCl at 400°C for 10mins without Applying: (a) Photographs of sample and (b) Intensity vs. Raman Shift signal with deconvolution results. The cross and arrow on (a) show where we got Raman Spectroscopy (b)

Center Grvty (cm ⁻¹)	Peak Type	FWHM (cm ⁻¹)	Max Height (a.u.)	Peak Area
1395.712	Lorentz	401.388	510.413	275684.064
1581.050	Lorentz	18.099	5047.047	142664.527
2710.956	Lorentz	62.299	1988.039	186943.885
2210.762	Lorentz	2634.658	411.297	736851.381

Table 4.3: Fitting results for TiC treated at 400°C for 10 minutes without applying voltage.

4.6 Characterization of TiC Substrate Treated in Ar gas in LiCl-KCl at 400°C at 3V for 10 Minutes by Raman Spectroscopy (Sample 2)

Figure 4.7(a) shows pictures of two sides of the sample treated in LiCl-KCl at 400°C. As shown in Figure 4.7(b) D and G band were located at 1366 and 1582cm⁻¹.

Compared to the reference results, I_D/I_G increased to 0.8 and the peaks are boarder which is also can be verified from table 4.4 that FWHM and the peaks area of this sample dramatically increased, which means that the structure of synthesized CDC by this process is more disordered than graphite structure. According to Section 2.6, the structure consists of NCG and a-C.



Figure 4.7: TiC treated at 400°C and 3V for 10 minutes: (a) Photographs of sample and (b) Intensity vs. Raman Shift signal with deconvolution results. The cross and arrow on (a) show where we got Raman Spectroscopy (b)

Center Grvty (cm ⁻¹)	Peak Type	FWHM (cm ⁻¹)	Max Height (a.u.)	Peak Area
1366.434	Lorentz	192.179	6474.948	1817197.661
1582.155	Lorentz	120.899	7974.661	1459199.262

Table 4.4: Fitting results for TiC treated at 400°C and 3V for 10 minutes in inert gas.

4.7 Characterization of TiC Substrate Treated in LiCl-KCl at 400°C and 3V for 10mins in Open Air by Raman Spectroscopy (Sample 3)

Due to relatively low operate temperature (400°C), electrolysis was done in open air. As shown in Figure 4.8(a), it is evident that the substrate material was etched, and the carburized layer may be eaten through because of the exposed metallic area. Therefore, another run was done for a shorter time in the next experiment.

In this Raman pattern, D and G band are at 1363 and 1582 cm⁻¹, respectively. 100% Lorentzian deconvolution was done by OriginLab[66].

Compared to sample 2 treated in inert atmosphere, D band becomes broader which is also obtained from larger FWHM, I(D)/I(G) increased to 1.07, which means a more disordered structure contains NC graphite and a-C is formed through this process as discussed in Section 2.6.



Figure 4.8: TiC treated at 400°C and 3V for 10 minutes: (a) Photographs of sample and (b) Intensity vs. Raman Shift signal with deconvolution results. The cross and arrow on (a) show where we got Raman Spectroscopy (b)

Center Grvty (cm ⁻¹)	Peak Type	FWHM (cm ⁻¹)	Max Height (a.u.)	Peak Area
1362.892	Lorentz	298.393	9097.751	3599771.952
1581.763	Lorentz	103.381	8463.734	1291938.857

Table 4.5: Fitting results for TiC treated at 400°C and 3V for 10 minutes in open air.

4.8 Characterization of TiC Treated in LiCl-KCl at 400°C and 3V for 1min in Open Air by Raman Spectroscopy and SEM (Sample 4)

The treated and cleaned surfaces of the TiC sample processed at 400°C and 3.V for 1 minute in open air is shown in figure 4.9(a) and (b). The secondary electron SEM image is beneficial for inspection of sample's topography, as can be seen in figure 4.9(b), the rough surface has been visibly etched and converted to CDC which was confirmed by Raman spectroscopy as can be seen in figure 4.9(c).

Compared to sample 3, G position shifts left a little bit, ID/IG increases to 1.26, which indicates that the structure of synthesized CDC under this condition is more disordered that that of sample 3.

Figure 4.10 shows EDS quantitative analysis results of the sample which indicates that the deposits are composed of the elements C, O, Cl, K, Ti as well as a little amount of Na. EDS detectors cannot detect presence of elements with atomic number less than 4, because windows in front of the Si(Li) detector can absorb low-energy X-rays. So, EDS cannot detect element Li. Atomic percentage of C is the highest, then is Ti which is from substrate material. Elements Cl and K are from LiCl-KCl molten baths.







Figure 4.9: TiC treated at 400°C and 3V for 1 minute: (a) Photographs and (b) secondary electron SEM image of sample and (c) Intensity vs. Raman Shift signal with deconvolution results. The cross and arrow on (a) show where we got Raman Spectroscopy (c)

Center Grvty (cm ⁻¹)	Peak Type	FWHM (cm ⁻¹)	Max Height (a.u.)	Peak Area	
1366.609	Lorentz	286.559	27099.436	1.05121E7	
1568.263	Lorentz	143.971	21585.141	4497129.409	

Table 4.6: Fitting results for TiC treated at 400°C and 3V for 1 minute in open air.

					Spe	ctrum 1
1 1 2 3 4	-	 6	7	8	<u>1</u>	ייייד 10
Full Scale 1596 cts Cursor: 0.000 keV						keV

Element	App conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	31.21	0.9695	32.35	0.32	62.17
O K	1.36	0.2881	4.72	0.39	6.84
Na K	0.16	0.9346	0.17	0.05	0.17
Cl K	1.94	0.9373	2.08	0.08	1.36
K K	0.94	1.2376	0.76	0.07	0.45
Ti K	53.64	0.8953	60.02	0.38	29.01

Figure 4.10: EDS analysis of TiC treated at 400°C and 3V for 1 minute in open ai

4.9 Theoretical Thickness of Synthesized CDC

The thickness of synthesized CDC by electrolysis of TiC in LiCl-KCl at 400°C and 3V for 1min in open air was estimated by calculation:

Average current through electrolysis process is 0.14Amps

0.14Amps = 0.14Coulomb/s

Q = 0.14 x 60 Coulombs = 8.4 Coulombs

 $n_e = Q/F$

Here, ne is amount of electron, F is Faraday constant which is 96485 Coulombs/mole.

$$n_{e} = \frac{8.4}{96485} \text{ mole} = 8.71 \text{ x} 10^{-5} \text{ mole}$$
$$\text{TiC} + 4\text{Cl}^{-} = \text{TiCl}_{4} + \text{C} + 4\text{e}^{-}$$
$$N_{c} = \frac{1}{4} n_{e} = 2.18 \text{ x} 10^{-5} \text{ mole}$$
$$M_{c} = 2.18 \text{ x} 10^{-5} \text{ mole} \text{ x} 12 \text{ g/mole} = 2.61 \text{ x} 10^{-4} \text{ g}$$
$$\rho_{c} = 2.26 \text{ g/cm}^{3}$$
$$V_{C} = \frac{2.61 \text{ x} 10^{-4}}{2.26} \text{ cm}^{3} = 1.15 \text{ x} 10^{-4} \text{ cm}^{3}$$
$$D = \frac{V}{A} = \frac{1.15 \text{ x} 10^{-4}}{0.8} \text{ cm} = 1.44 \text{ x} 10^{-4} \text{ cm} = 1.44 \mu m$$

4.10 Interpretation of results

To sum up, experiment conditions and results of these 6 samples are listed in table 4.7. First, due to low conductivity of SiC, the first run results in a low current which is 0.04 Amps, after using carburized Ti6Al4V to replace SiC sample, the average current apparently increased.

Second, 100% Lorentzian deconvolution was done on Raman results by OriginLab[66]. D and G peaks were detected for these 6 samples, since $I_D/I_G = 0$ and there is no D band for pure graphite structure, sharp G bands and low I_D/I_G ratios for reference and blank comparison results indicate an ordered graphite structure which is from graphite powder stuck in the surface during carburization process. For the other four samples treated by electrolysis, I_D/I_G ratios become larger, D and G bands are broader which can be concluded from increased FWHM and area, meaning CDC are obtained through electrolysis and the structures are more disordered than graphite. Besides, SEM and EDS analysis were carried out for sample 4, rough surface and high C content indicate that the surface is etched and has been visibly converted to CDC.

Also, theoretical thickness of Sample 4 was carried out which is 1.44 μm , nevertheless, the result may not very accurate since (a) CDC has a porous structure of which the density may differ from that of element carbon used in the calculation; (b) we assumed that every 4mole Cl⁻ react with 1mole TiC to generate TiCl₄ and CDC in calculation, whereas the stoichiometry may be different in the real reaction, 1.44 μm is the maximum theoretical thickness of sample.

	Sample #	Sample 1	Reference results	Blank comparison	Sample 2	Sample 3	Sample 4
Substrate Material		SiC	Carburized Ti6Al4V	Carburized Carburized Ti6Al4V Ti6Al4V		Carburized Ti6Al4V	Carburized Ti6Al4V
	T (°C)	825	/	400	400	400	400
V	Voltage (V)	3	/	/	3	3	3
Т	Time (Mins)	30	/	10	10	10	1
A	Atmosphere	Ar gas	/	Ar gas	Ar gas	open air	open air
	Salts bath	Pure NaCl	/	LiCl-KCl	LiCl-KCl	LiCl-KCl	LiCl-KCl
Dec	convolution R ²	0.972	0.988	0.980	0.911	0.995	0.994
(Current (A)	0.04	/	/	0.12	0.10	0.14
D peak	position (cm ⁻¹)	1353	1345	1396	1366	1363	1367
	FWHM (cm ⁻¹)	146	44	401	192	298	167
1	Area	7.35E+05	1.21E+05	2.76E+05	1.82E+06	3.60E+06	1.05E+07
G peak	position (cm ⁻¹)	1589	1578	1581	1582	1582	1568
	FWHM (cm ⁻¹)	93	25	18	121	103	144
	Area	4.09E+05	1.81E+05	1.43E+05	1.46E+06	1.29E+06	4.50E+06
	I _D /I _G	1.16	0.39	0.10	0.80	1.07	1.26

Table 4.7 Summarized experiment conditions and results of 6 samples

At last, compared to experiments done under Ar atmosphere, it is more convenient to do electrolysis in open air, since after preparing salts melt, several electrolysis processes can be directly and continuously done without cooling the system down, assembling the samples and redrying the system each time before electrolysis. Meanwhile, there is no need to worry about product loss or oxidation reaction owing to infiltrated air.

5. CONCLUSION

In conclusion, this study has demonstrated the following:

- SiC-CDC was synthesized using reactive anode electrolysis in pure NaCl electrolyte under Ar atmosphere, which generated a small current due to low conductivity of SiC. After that, a TiC layer was made by carburizing at 1000°C for 24h, TiC-CDC was produced in open air by electrolysis in molten LiCl-KCl which has a much lower melting point (353°C) than pure NaCl (801°C) or NaCl-KCl (657°C) previously used in Mika's work[4]. Open air operation makes the process more efficient and convenient than ones done in inert gas.
- Both broader peaks and larger ratios of intensity (I_D/I_G) indicate a more disordered structure than pure graphite. It was demonstrated that CDCs with structures which may contain NCG and a-C were produced.
- Theoretical thickness of Sample 4 was roughly estimated by calculation, which is about $1.44 \ \mu m$.

Recommendations for future studies are as follows:

- Cyclic Voltammetry can be done to determine oxidation-reduction reactions during electrochemical process and the potential at which redox reactions occur. The optimal experiment conditions such as temperature, voltage and time can be studied to make the process more efficient.
- Tribological properties of prepared CDC can be tested to promote its applications in biochemical field. Study on pore size and distribution of products would benefit applications such as EDLCs and batteries.

• Real thickness of synthesized CDC layer needs to be measured and compared with theoretical value, which may make it possible to control thickness of products by tuning experiment conditions such as voltage, time and temperature.

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EDUCATIONAL BACKGROUND

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Master of Science — Materials Science (Civil and Material Engineering Department)

Beijing University of Chemical Technology (BUCT), Beijing, China 09/2012 - 06/2016

Bachelor of Engineering — Polymer Science and Engineering

RESEARCH EXPERIENCE

Master Thesis, UIC, 12/2017 – 08/2019

Synthesis of Carbide Derived Carbon (CDC) by Electrolysis in Molten Chlorides in Open Air

- Studied properties of a various of molten salts.
- Optimized the experiment setup and its testing condition.
- Surface modification of Ti alloys (solid carburization).
- Familiar with use of Raman Spectroscopy and analysis of CV, SEM and XRD results.

Under-graduate Thesis, BUCT, 12/2015 - 05/2016

Synthesis of Graphene/Ni(OH)2 Composite and its Application in Supercapacitors

- Studied preparation of graphene oxide by Modified Hummers' Method
- Successfully fabricated the graphene composites by chemical reduction processes.
- Characterized prepared materials by Raman spectroscopy, SEM and XRD.
- Tested electrochemical properties of products by CV, Galvanostat Cycling at different

current densities, Electrochemical Impedance Spectroscopy (EIS).

INTRESTS

Painting, swimming, playing guitar and learning new things.