

Electrochemical Reactions on Graphite Cathodes in High-Voltage Capacitors

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Abstract

In a recent CARTS contribution, we demonstrated that activated carbon in the form of graphite printed onto titanium substrates is a viable cathode material for high-voltage, implantable cardioverter-defibrillator capacitors. In this paper, we report on the electrochemical properties of the graphite-on-titanium cathode in aqueous electrolytes.

We have characterized electrochemical reactions on the graphite cathode as a function of electrode potential and electrolyte pH. In the potential range from -0.1 to about -0.7 V, the reduction of molecular oxygen to hydrogen peroxide was observed. This reaction is diffusion limited and dependent upon the oxygen concentration at the electrode-electrolyte interface. It controls the self-discharge of this electrode. At potentials more negative than -0.7 V and at pH values of 5 and larger, the hydrogen evolution reaction was the dominant charge transfer reaction.

We conclude that none of these reactions impact the performance of the capacitor, provided that the cathode is properly designed.

I. Introduction

In implantable defibrillators, liquid-electrolytic, high-voltage capacitors are used to generate life-saving electrical pulse therapy upon detection of severe arrhythmias. A strong pulse transmitting about 10 – 40 J of energy at a potential difference of 600 to 800 V will be delivered directly into the heart tissue. Two liquid electrolyte capacitor technologies are currently in use: One is based upon stacks of anodized Al plates sandwiched between Al cathodes (1, 2). In the other, anodized, porous Ta and a coating of RuO₂ serve as anode and cathode materials, respectively (3, 4).

In a recent CARTS contribution, we have demonstrated that a coating of graphite on titanium substrates constitutes a robust cathode suitable for both anode technologies currently in use (5, 6). In this cathode, as in almost all carbon-based electrode systems, charge is stored predominantly by virtue of accumulation in the electrochemical double layer at the cathode-electrolyte interface (7). Hence, the surface charge-density is a function of the electrode potential. The capacitance is proportional to the surface area accessible by the electrolyte. Ideally, charge storage in the double layer is entirely non-Faradaic. In practice, however, charge transfer reactions are expected in most electrode-electrolyte systems, particularly at high charge densities or polarization potentials. Indeed, the self-discharge process of a liquid electrolytic capacitor at open circuit is largely due to Faradaic currents across the double layer (8, 9). Hence, characterizing and understanding these charge-transfer reactions

enhances the operational safety of the capacitor system and may enable technological improvements. In a previous contribution, we reported on the Kolbe reaction occurring on anodically charged Ta anodes in aqueous electrolytes (9). In the present proceedings, we will provide details on electrochemical charge transfer reactions at the cathodically polarized graphite-electrolyte interface. Specifically, we will address the reduction of dissolved oxygen and the hydrogen evolution reaction.

II. Charge transfer reactions in the cathodic polarization region

a.) General aspects of charge transfer reactions

The overpotential U and the current, i driving charge transfer reactions, are logarithmically related by the Tafel equation:

$$U = a + b \log i \quad (E1)$$

In equation E1, U is the overpotential (i.e., the difference between the cell potential and the equilibrium potential), a denotes a constant and b is the so-called Tafel slope, which is stated in V per logarithmic current decade. The Tafel slope b in E1 can be experimentally determined by controlling the electrode potential and measuring the cell current. If a one-electron transfer from the electrode to an adsorbed species controls the overall reaction, the Tafel slope should theoretically be:

$$b = 2.3 RT/(0.5F) = 0.118 \text{ V (at 298 K)} \quad (E2)$$

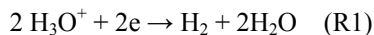
In E2, R is the ideal gas constant (8.3 Joule per Kelvin per mole), T is the temperature in K and F is the Faraday (=96485 C). Alternative to equation E1, the relation between cell current and overpotential may be expressed as an Arrhenius rate equation:

$$i = i_0 \exp(cU/RT) \quad (E3)$$

Here, c is a constant for a given charge transfer reaction and i_0 denotes the exchange current density. Experimentally, it is determined by extrapolating the Tafel line to the equilibrium potential and determining the corresponding current density. i_0 signals the ability of a given electrode material to catalyze a given charge transfer reaction.

b.) Hydrogen evolution reaction in acidic electrolytes on graphite electrodes

The hydrogen evolution reaction (HER) is one of the most studied reactions in electrochemistry. Conway wrote a wonderful review encompassing both the historical and the current understanding of HER (10). In the overall reaction of HER in acidic media, two hydronium ions decompose on the electrode surface to generate one hydrogen and two water molecules. It is represented as follows:



Reaction R1 is thought to proceed in two consecutive steps. The first step is always the proton discharge:



M stands for the substrate surface and H_{ad} denotes a hydrogen atom adsorbed on the substrate surface. Following the proton discharge, molecular hydrogen may be generated, for example

by the reaction between two adsorbed hydrogen atoms. If the initial proton discharge (step 1) controls the overall reaction, the Tafel slope is given by equation E2, i.e., b should be found in the vicinity of 120 mV at 25 °C. Experimental results on HER on graphite were summarized in the book by Kinoshita (11). The exchange current densities are quoted to be in the range of 10^{-6} to 10^{-5} mA / cm² for the different crystallographic planes of graphite (12, 13). The Tafel slopes are found between 120 and 180 mV (12, 13). Hence, the initial single charge proton discharge step given by equation E2 is likely the rate limiting step.

c.) Oxygen reduction in acidic electrolytes on graphite electrodes

The bulk of the work on oxygen reduction on graphite was performed in alkaline media (14, 15), but some results are available for acidic media (16). The overall reaction is the reduction of molecular oxygen to peroxide. It is found at low cathodic polarizations and it is strongly dependent upon diffusion of molecular oxygen to the electrode. The proposed mechanism consists again of several steps: The first is the adsorption of molecular oxygen, the second the electronation of the adsorbed oxygen. Finally, the adsorbed, charged oxygen species is protonated and desorbs. The reported Tafel slope is again close to 120 mV, indicating that the one-electron transfer from the electrode to the oxygen molecule is the rate limiting step.

III. Experimental section

Sample cathodes were prepared as described earlier (5). Briefly, graphite was ink-jet printed onto a titanium substrate using a graphite powder suspension in water as the ink and a piezo-electrically operated micro-dosing valve as the print engine. Subsequent processing of the

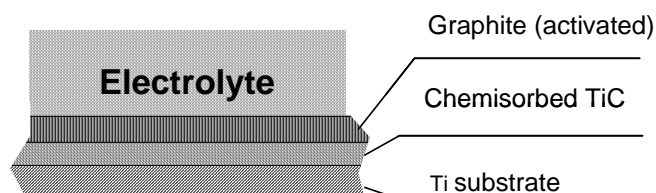


Figure 1. The structure of the graphite cathode

printed titanium sheet in a vacuum annealing step at temperatures between 600 °C and 1000 °C creates a titanium carbide layer, which is sandwiched between the graphite cathode and the titanium substrate. This intermediate layer provides good

electrical conductivity from the titanium to the graphite at the cathode-electrolyte interface because TiC has a very high electronic conductivity. It also provides a good bond of the graphite layer to the substrate because TiC is chemisorbed to the titanium. The substrate, the intermediate TiC layer and the carbonaceous coating are sketched in Figure 1. Before use as a capacitor electrode, the carbonaceous coating is thermally activated in air at temperatures between 100 °C and 600 °C in a convection furnace. Activation increases the accessible surface area of the electrode by a factor of about 10, as determined from capacitance measurements. The thickness of the coating was on the order of 10 μm, the capacitance at 0.1 Hz was found to be about 20 mF/cm².

For all electrochemical measurements a Solartron SI 1260 impedance / gain phase analyzer in conjunction with the SI 1287 electrochemical interface was used. A three-electrode configuration consisting of the working electrode (graphite cathode), a 2 x 2 cm² Pt counter electrode and a reference electrode (Ag / AgCl (saturated KCl)) was employed. All experiments were performed at body temperature (37 +/- 2 °C). Tafel slopes were obtained

potentiostatically by recording the current at a series of controlled potentials. For any given point, the potential was held for 15 min and the current was logged in 1 second intervals. The current values reported represent the average current of the 100 seconds at the end of the 15 min period. In this way, the contributions of double layer charging to the overall current can be eliminated.

Various electrolytes were used to explore the electrode at different pH values: For pH 1, an aqueous solution of H_2SO_4 , for pH 7 a saturated solution of NaCl in water and for pH 11.3 an ammonium hydroxide solution in water. The electrolytes with a pH of 4 and 5 were proprietary formulations selected from the formulations disclosed in US patent 7,081,141 (14).

IV. Results and discussion: Electrochemistry of graphite coatings on Ti substrates

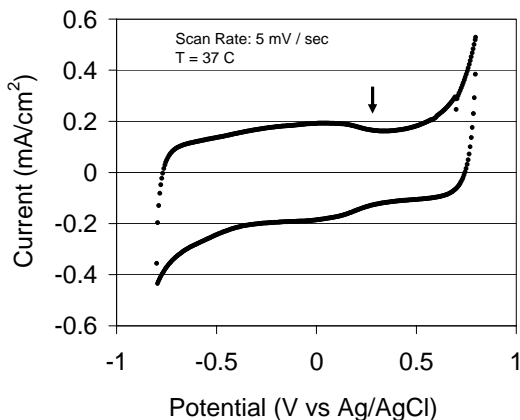


Fig. 2 Cyclic voltammogram of the graphite cathode. Oxygen evolution is expected at potentials in excess of +0.75 V, hydrogen evolution for potentials in excess of -0.75 V. The arrow marks the position of the open circuit potential at about +0.3 V.

indicated by the arrow.

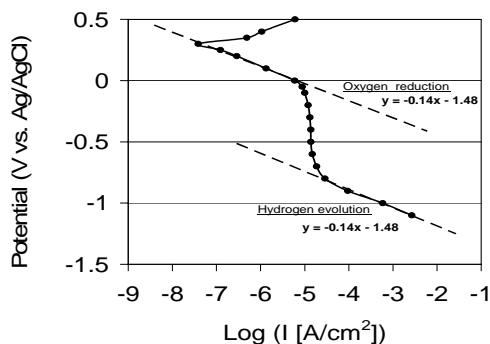


Fig. 3 Tafel plots of the graphite-on-Ti electrode obtained at $T = 37\text{ }^\circ\text{C}$ and $\text{pH} = 5$. One linear region with a slope of 138 mV is indicated in the low polarization voltage regime. A second linear region is identified at potentials more negative than -0.7 V. $T = 37 \pm 2\text{ }^\circ\text{C}$. $\text{pH} \sim 5$

a.) Cyclic voltammetry

Figure 2 shows a cyclic voltammogram of the graphite-on-Ti electrode. The rectangular shape of the voltammogram over a wide potential window ranging from about -0.7 V to about +0.7 V is indicative of a good capacitor. Stable capacitance is maintained within this potential window, as indicated by the almost constant charging current. In this so-called double layer region, non-faradaic charging currents are expected to dominate. Not so outside of this potential window: Hydrogen evolution likely begins at potentials more negative than -0.7 V, and oxygen evolution at potentials in excess of +0.7 V. The open circuit – or equilibrium - potential is

It is typically found around +0.3 V. In the following, the potential region from the open circuit potential down to the hydrogen evolution potential will be examined in greater detail. It is this potential region which the cathode potential likely encompasses during charging of the capacitor anode.

b.) Current-voltage measurements: oxygen reduction and hydrogen evolution

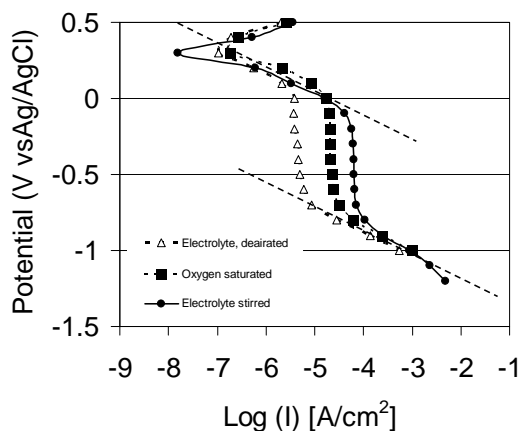


Fig. 4 Tafel plots of the graphite cathode. Open triangles: de-airated electrolyte (Ar bubbling for 2h). Full squares: oxygen saturated electrolyte (O₂ bubbling for 2 h). Full circles: Stirred electrolyte, no pre-treatment. T = 37 +/- 2 °C. pH ~ 5.

Figure 3 shows the result of a potentiostatic Tafel slope experiment. The equilibrium potential of the graphite-on-Ti electrode at +0.3 V is clearly evident. One linear region is identified in the lower polarization voltage regime just below the equilibrium potential and a second one at a polarization voltage more negative than -0.7V. Furthermore, the current density regime around 10⁻⁵ A/cm² stands out because here, the cell potential changes dramatically by almost 0.75 V. Evidently, the current value of 10⁻⁵ A/cm² represents some form of limiting current.

Diffusion plays a major role in the reduction of dissolved molecular oxygen, as was sketched in section II above. In addition, the Tafel-slope for this process was found in the vicinity of 120 mV at 25 °C (14, 16). Therefore, it appears likely that the Tafel slope of 140 mV in the low cathodic potential regime and the diffusion-limited current are associated with the reduction of dissolved molecular oxygen (a Tafel-slope value slightly higher than 120 mV is expected in part because this measurement was performed at 37 °C). If this speculation were true, the value of the limiting current density should be strongly dependent upon the concentration of oxygen in the electrolyte. Indeed, Figure 4 shows that saturating the electrolyte with oxygen, stirring the electrolyte and depleting the electrolyte of oxygen changes the limiting current density by almost an order of magnitude. In addition, the presence of peroxide upon polarizing the graphite electrode to -0.5 V was directly validated by the color change of a peroxide test strip (18). A concentration of 2mg/l was indicated. Furthermore, the measured value of the limiting current can be used to estimate the oxygen saturation concentration, which can then be compared to the known value. The limiting current density for a one-electron charge-transfer reaction is given by (19):

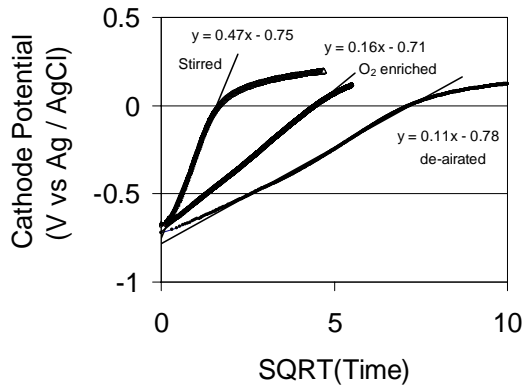


Fig. 5 Self-discharge curves of graphite-on-Ti electrodes in stirred electrolyte, in oxygen enriched electrolyte and in de-aired electrolyte. The electrode discharge takes the longest time in the de-aired electrolyte (Note the square-root of time scale).

This finding has implications for the self-discharge of the graphite-on-Ti electrode in a capacitor (see Figure 5): Diffusion-controlled self discharge is expected to be linear with the square root of time. Figure 5 shows that self-discharge is indeed linear with the square root of time down to a potential of about 0V. This is consistent with Figure 4, where it could be seen that the diffusion-limited current sets in about 0 V. Figure 5 also demonstrates that the rate of self-discharge just depends on the oxygen transport rate to the electrode-electrolyte interface. These data suggest that in an actual capacitor, low oxygen concentrations should be maintained in the electrolyte in order to avoid accelerated self discharge of the cathode, specifically also at low to moderate cathodic polarizations. Low to moderate cathode polarizations are certainly encountered while the capacitor anode is charged and cannot be avoided by the capacitor designer.

In contrast, polarizations more negative than -0.7 can be avoided by proper dimensioning of the cathode capacitance. In this potential range, a linear Tafel slope of 140 mV is indicated in Figure 3. Charge transfer reactions in this potential region are likely dominated by the hydrogen evolution reaction (HER). If so, equation E2 of section II would suggest that the initial proton discharge step (one-electron transfer) is the rate limiting step. A variation of the electrolyte pH value should leave the Tafel slope largely unaffected but bring about characteristic changes in the exchange current density or, in other words, change the onset of the reaction on the potential scale. Figure 6 demonstrates this: for a pH of 1 (open squares, H_2SO_4) a Tafel slope of 120 mV is found, and the exchange current density is projected to be at about 10^{-8} A/cm². For pH 7 (open triangles, NaCl), the Tafel slope is 140 mV and the exchange current density is projected to about 10^{-13} A/cm². Given that the highest exchange current densities for HER are found on Pt-group metals with values around 10^{-3} A/cm², the activity of the graphite-on-Ti electrode may be classified as low to moderate. The onset of HER on the potential scale was extracted from current-potential traces such as those shown in Figure 6 by defining the potential E_c at the cross-over of the Tafel line with the extrapolated line representing the limiting current as the onset of HER. In Figure 7, the cell potentials E_c are plotted as a function of pH. As shown by Bockris and Reddy (19), this plot should be a straight line given by:

$i_L = (D F/d) c_O$ (E4) D is the diffusion coefficient, d is the diffusion layer thickness and c_O is the oxygen saturation concentration. Using the i_L value found in the oxygen-saturated electrolyte ($= 2.1 E-5$ A/cm²) together with common values for D ($=3.2E-5$ cm²/s) and d ($=0.05$ cm), an oxygen saturation concentration of $c_O = 3.4E-7$ Mol/cm³ or about 10 mg / l is calculated. This value is in good agreement with the actual oxygen saturation concentration found in water at 40 °C under ambient atmospheric pressure. This estimate, the measured Tafel-slope and the peroxide test strip result all confirm that oxygen reduction is the dominant charge transfer reaction in the potential regime from the equilibrium potential to about -0.7 V.

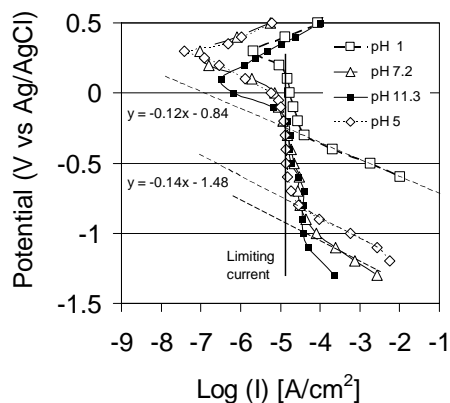


Fig. 6 Tafel plots of the graphite-on-Ti electrode obtained at $T = 37\text{ }^{\circ}\text{C}$ and various pH values as indicated in the legend. The Tafel slope associated with the hydrogen evolution remains at about 120 mV for pH values 1, 5 and 7. In the base (pH = 11.3) it becomes somewhat larger (180 mV). The onset of hydrogen evolution is marked by the crossing of the Tafel-line with line marking the limiting current. $T = 37 \pm 2\text{ }^{\circ}\text{C}$.

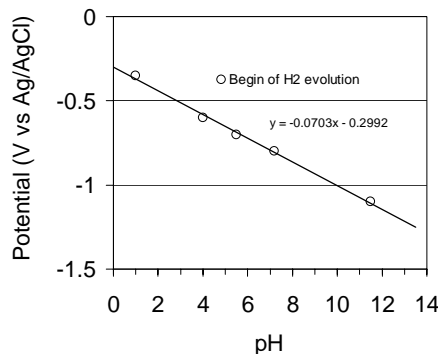


Fig. 7 The onset of HER as a function of pH value. When measured against a normal hydrogen electrode, a straight line with a slope of -0.058 and zero offset is expected for $T = 25\text{ }^{\circ}\text{C}$. For $T = 37\text{ }^{\circ}\text{C}$ and against a Ag/AgCl reference electrode, the slope is somewhat higher and the offset should be about 0.23 V.

$$E_c = -0.059 \text{ pH (E5)}$$

The plot in Figure 7 agrees quite well with the prediction of equation E5 considering that the experiments were performed at $37\text{ }^{\circ}\text{C}$ and an Ag / AgCl reference electrode was used in the experiments. This electrode is offset to NHE by 0.235 V. Therefore, charge transfer in the potential region more negative than -0.7 V is almost certainly due to HER, with the initial proton discharge step being the rate limiting one.

V. Conclusions

Graphite-coated titanium electrodes provide high capacitance cathodes for high voltage capacitors. Oxygen reduction is the dominant charge transfer reaction in the low to moderate polarization voltage regime ranging from the equilibrium potential of 0.3 V vs. Ag / AgCl to about -0.7 V vs. Ag / AgCl. This potential regime is likely encompassed when the anode is charged to high voltage. The reaction rate is diffusion-limited and a function of the oxygen concentration. The reaction dominates the self discharge of this electrode.

The hydrogen evolution reaction was found to be the dominant charge transfer reaction in the potential regime more negative than -0.7 vs. Ag/AgCl and at a pH of 5 and above. The associated exchange current densities signal a low to moderate activity of the graphite-on-Ti electrode towards the hydrogen evolution reaction.

None of these reactions impact the performance of the capacitor, provided that the cathode capacitance is properly dimensioned and the oxygen concentration is kept well below the saturation concentration.

IV. References

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