

Electrochemical corrosion investigations on metal doped a-C:H coatings for bipolar plates in redox-flow batteries
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A contributing factor regarding the volumetric power density of a redox flow battery stack is the development of thin and cost reduced bipolar plates. One promising approach is the use of coated metals as bipolar plate material. Metals offer adequate mechanical stability whereas the coating should also meet the electrochemical requirements. These requirements are low corrosion currents in the acidic media as well as high overpotential against hydrogen and oxygen evolution. A boron doped diamond coating deposited by chemical vapor deposition exhibits extraordinary corrosion behavior and high overpotential for hydrogen and oxygen evolution. But their use as bipolar plate material is limited by the use of expensive niobium as substrate material. Therefore metal doped a-C:H coatings are regarded as promising alternatives. The metal dopants are necessary to achieve high conductivities in the order of ~ 100 S/cm [1] in other respects to the low-conductive a-C:H coating. Elements such as titanium, tungsten, chromium or vanadium are investigated as suitable dopants. For the corrosion measurements all a-C:H:Me coating samples were treated after the following procedure: Prior to the measurement the samples were cleaned with isopropanol, rinsed with deionized water and dried in an air stream. The electrochemical tests of each sample starts with cathodic polarization for 5 min. Afterwards the OCV is taken for 30 min until it reaches steady state. A 3-electrode corrosion cell filled with 100 ml 2 M H₂SO₄ provides the test environment for the material specimen. For the potentiodynamic measurement seen in figure 1 the potential is varied with a sweep rate of 5 mV/s from OCV in cathodic direction until $-500 \mu\text{A}/\text{cm}^2$ is reached. Then the voltage is swept in anodic direction until a current of $500 \mu\text{A}/\text{cm}^2$ and back in cathodic direction until -300 mV vs. OCV. For the comparison of different materials only the middle part of the current graph of the potential sweep is taken into account. The stability of the coating is analyzed by 200 cycles (see figure 2) in potential range of -0.6 V vs. NHE and 1.4 V vs. NHE.

As it can be seen in figure 1 chromium, vanadium and tungsten doped coatings show lower corrosion current for a wide potential range on the anodic branch of the graph compared to the titanium doped DLC coating. Regarding the hydrogen evolution potential the titanium doped DLC film possess the highest overpotentials of all tested coatings (see figure 1).

One of the major problems of coatings, used to protect metals in harsh environments are defects. These defects can be formed during the deposition process or can result from degradation during the electrochemical tests [2]. Therefore first tests were done with a scanning electrochemical microscope [2] (SECM) on a a-C:H:Ti sample. Figure 3 shows current densities plotted over a $1000 \mu\text{m}^2$ area of a new sample. The blue parts show higher cathodic currents than the rest of the sample. Most certainly these higher current densities are due to pinhole defects which result from the PVD coating process. The electrochemical characterization of the coatings is accompanied by microscopic analysis and drop shape

analysis to record the surface modification of the specimens during electrochemical loading.

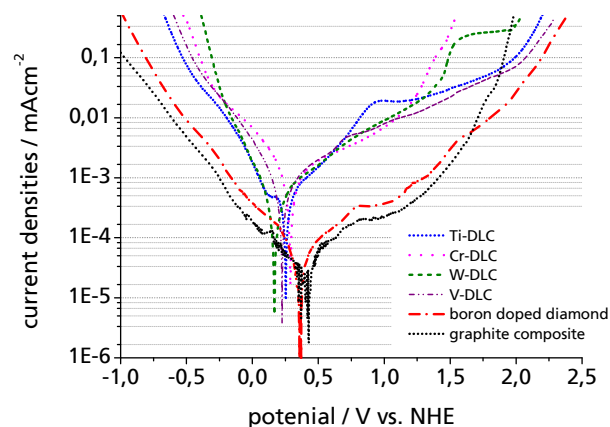


Figure 1: Potentiodynamic measurements of different a-C:H:Me coatings on 1.4301; $dU/dt = 5$ mV/s, $|i_{\text{max}}| = 500 \mu\text{A}/\text{cm}^2$

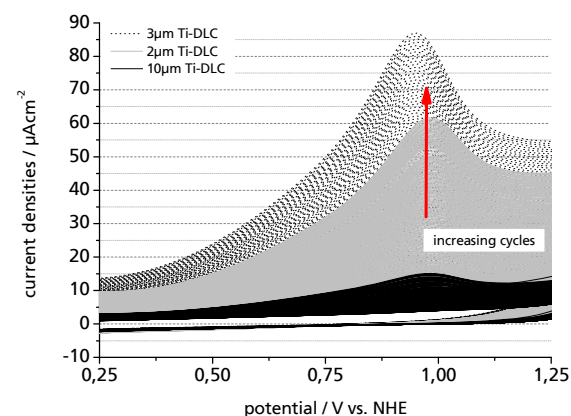


Figure 2: Cyclovoltammogram of a-C:H:Ti of different thicknesses on TiAl6V4 substrate in 2 M H₂SO₄; $dU/dt = 10$ mV/s

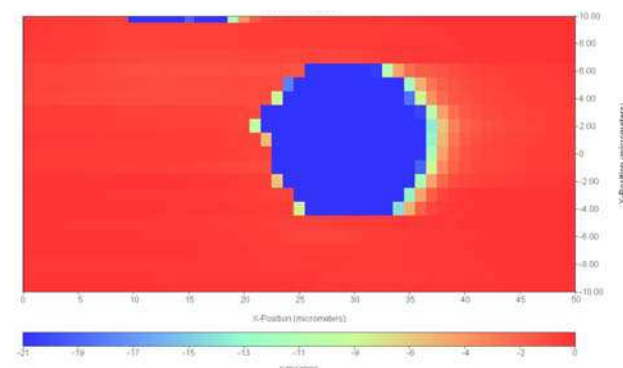


Figure 3: SECM investigation on $1000 \mu\text{m}^2$ of a $3 \mu\text{m}$ a-C:H:Ti coating on 1.4301, time: 1200 s; 10 mM KI and 100 mM KCl, $\varphi = -0.2$ V vs. NHE; Results published with the courtesy of Uniscan Instruments Ltd and Bio-Logic SAS

Acknowledgements

We thank Daniel Lonsdale (Uniscan Instruments Ltd) and Nicolas Murer (Bio-Logic SAS) for the SECM measurement. We also acknowledge the financial support of this work by the Fraunhofer MEF Project founding.

References

- [1] Mawdsley, J et al.; FY 2011 Annual Progress Report DOE Hydrogen and F-Cell Program (2011) 867-871
- [2] Lillard, R. S. et al.; Corrosion Science, Vol. 39, No. 9 (1997) 1601-1624
- [3] Davoodi, A et al.; Electrochemical and Solid-State Letters, Vol. 8, No. 6 (2005) B21-B24