

Electroreduction of Oxygen on Electrochemically Deposited Palladium Coatings on Glassy Carbon

Heiki Erikson^a, Madis Liik^a, Ave Sarapuu^a, Jekaterina Kozlova^b, Väino Sammelselg^{a,b}, Kaido Tammeveski^{a,*}
^a*Institute of Chemistry, University of Tartu, Ravila 14A, 50411 Tartu, Estonia*

^b*Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia*

*kaido.tammeveski@ut.ee

In the pursuit to find an alternative catalyst to replace Pt in polymer electrolyte membrane fuel cells Pd has received much attention. Palladium is a favored choice due to similar properties with platinum and oxygen reduction pathway is the same on both metals.¹

In this study, Pd was electrodeposited onto glassy carbon (GC) substrate at a constant potential varying the deposition time and the electrocatalytic activity of Pd/GC electrodes toward the oxygen reduction reaction (ORR) was compared with that of bulk polycrystalline Pd.²

The HRSEM micrographs show that after 300 s of Pd deposition there are small nanoparticles and some larger agglomerates. Increasing the deposition time resulted in formation of more agglomerates, but still some uncoated GC surface can be observed with some small Pd islands on it. The size of small Pd particles was in the range of 3 to 10 nm and larger agglomerates were up to 100 nm.

The electroreduction of O₂ on electrodeposited Pd/GC electrodes was studied in O₂-saturated 0.05 M H₂SO₄ using the RDE method. Single waved polarization curves were observed for all the electrodes studied (Fig. 1a).

Comparison of palladized electrodes shows that the specific activity (SA) slightly depends on the deposition time, being highest for 900 s (0.25±0.01 mA cm⁻²) and lowest for 300 s deposited Pd (0.19±0.04 mA cm⁻²). The SA value of 600 s deposited Pd coatings was similar to that of bulk Pd (0.24±0.02 mA cm⁻²).

The RDE results were analyzed using Koutecky-Levich equation and from the slopes of the corresponding plots the number of electrons transferred per O₂ molecule (*n*) was found. For 600 s and 900 s deposited Pd as well as for bulk Pd the *n* value was close to four, but for the lowest amount of Pd deposited on GC it was between 3.5 and 3.9. The mass-transfer corrected Tafel plots of O₂ reduction (Fig. 1b) exhibit two regions with different slope values: -60 mV dec⁻¹ and -120 mV dec⁻¹.

The ORR measurements were also carried out in 0.1 M KOH solution (Fig. 2a). In alkaline medium there was no dependence between SA and deposition time and Pd/GC electrodes possessed lower SA values than bulk Pd. 300 and 600 s deposited Pd catalysts had essentially the same SA values, 0.39±0.01 mA cm⁻² and 0.38±0.02 mA cm⁻², respectively. The SA for 900 s deposited Pd was 0.43±0.09 mA cm⁻² and for bulk Pd 0.48±0.02 mA cm⁻².

The number of electrons involved in ORR was found to be 4 for 600 s and 900 s deposited Pd as well as for bulk Pd. For 300 s deposited Pd the value of *n* was between 3.7 and 3.9 indicating that some peroxide is formed.

The mass-corrected Tafel plots (Fig. 2b) showed a single slope for 600 and 900 s deposited Pd and bulk Pd (-60 mV dec⁻¹), but for 300 s deposited Pd coatings two Tafel slope regions were determined (-60 and -120 mV dec⁻¹).

Studying the electrocatalytic properties of Pd-based catalysts is important to find replacement for expensive Pt-based catalysts and electrodeposited Pd may be utilized as a cathode material in low temperature fuel cells.

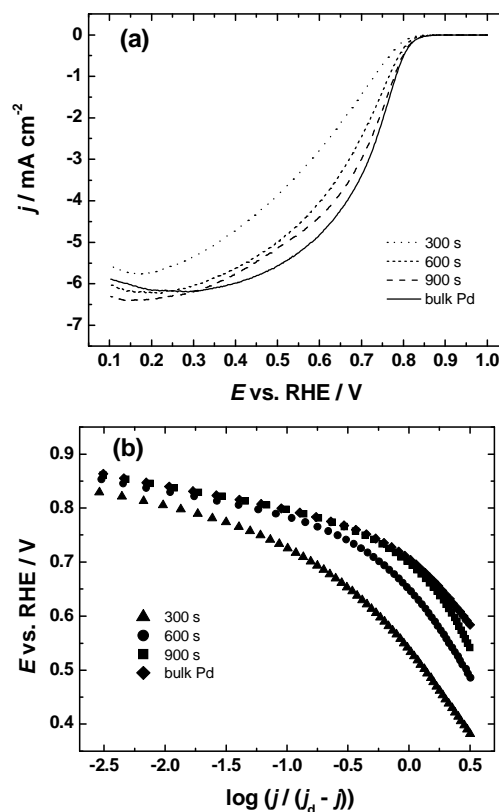


Figure 1. (a) Comparison of RDE voltammetry curves of ORR on Pd/GC and bulk Pd electrodes in O₂-saturated 0.05 M H₂SO₄ and (b) mass-transfer corrected Tafel plots for ORR in 0.05 M H₂SO₄. $\omega = 1900$ rpm, $v = 20$ mV s⁻¹.

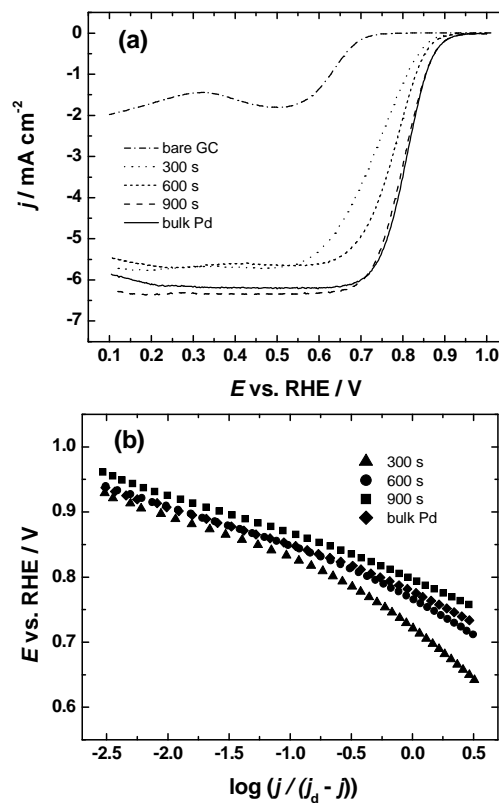


Figure 2. (a) Comparison of RDE voltammetry curves of ORR on Pd/GC and bulk Pd electrodes in O₂-saturated 0.1 M KOH and (b) mass-transfer corrected Tafel plots for ORR in 0.1 M KOH. $\omega = 1900$ rpm, $v = 20$ mV s⁻¹.

References

- [1] E. Antolini, *Energy Environ. Sci.*, **2**, 915, 2009.
- [2] H. Erikson, M. Liik, A. Sarapuu, J. Kozlova, V. Sammelselg, K. Tammeveski, *Electrochim. Acta*, <http://dx.doi.org/10.1016/j.electacta.2012.10.118>