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# Nitrate electroreduction on Pt in metatungstate-containing solution

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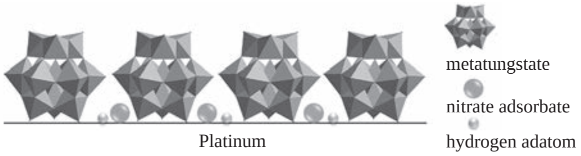
**Metatungstate Keggin anions are capable of catalyzing nitrate electroreduction on Pt at potential values preceding hydrogen evolution, which makes them a rare example among other anions since such a type of catalytic behavior has been usually observed exclusively for cations.**



The nitrate electroreduction is a very slow reaction,[1] so only few electrode materials provide reaching the diffusion limit in this reaction. Typical onset of nitrate reduction only rarely exceeds 0.2–0.3 V RHE (*i.e.* overvoltage of 0.6–0.7 V) even for the most active electrocatalysts. The available potential interval between the onsets of nitrate reduction and hydrogen evolution, if any, is rather narrow making complicated the analysis of reaction kinetics.

In the initial work,[2] the pronounced effect of the background anions on the kinetics of nitrate electroreduction on polycrystalline platinum was found. Later, the hypothesis of self-inhibition in this reaction by hydrogen adatoms on Pt was comprehensively grounded.[3–7] The experiments on Pt single crystals[1] also revealed the role of supporting anions. All reported experimental facts support the idea that the anions are harmful for the nitrate reduction, which proceeding *via* adsorption pathways.

On the contrary, various cations favor nitrate reduction on Pt. The cations even weakly absorbed on the Pt surface provide a sharp increase of nitrate reduction current on the Pt electrode below ~0.1 V of RHE.[4,6,7] The origin of this effect was considered for Cu adatoms[8] and many cations of non-transition metals.[9,10] From this point of view, one can hardly propose any unified concept to interpret the effects of various cations since their influence on reaction selectivity reveals different reaction pathways. In general, all the mechanistic ideas assume catalytic hydrogenation (chemical reaction of the second order in adlayer). In particular, the 'third body' effect and local effects of cations were supposed for nitrate bonding in adlayer.

At the best of our knowledge, tungstates are only one type of anion-based additives reported as causing a positive effect on nitrate reduction on platinum. The first observed example was tungstate-modified Pt, where a mixture of various isopolytungstate species was coadsorbed from acidic $Na_2WO_4$ solution.[11] Our group have recently reported[12] that metatungstate Keggin anion $[H_xW_{12}O_{40}]^{(8-x)-}$, in contrast with other isopolyanions, did not undergo any transformations in acidic medium during a formation of monolayers on the Pt surface. We observed that the currents of nitrate electroreduction at potentials below *ca*. 0.1 V RHE could be essentially increased in the presence of metatungstate isopolyanion, *i.e*. under reversible adsorption conditions.[12]

According to other reports,[13–18] this observation can be hardly associated with 'homogeneous electrocatalysis' of nitrate reduction by substituted heteropolytungstates. Such a process involves a mediating step in diffusion layer rather than at the surface. Moreover, substituting ions ($Cu^{II}$, $Ni^{II}$, and $Fe^{II}$) played a crucial role in the mediating step, while $W^{VI}/W^{V}$ redox transition demonstrated no effect on nitrate reduction.[18] All described observations[13–18] correspond to the negative RHE potentials and weakly acidic solutions, which maintains the stability of catalysts. In addition, no steady-state data have ever been presented for heteropolytungstates in the nitrate reduction process.

Here, we report new data for nitrate/metatungstate system and discuss the specific features responsible for electrocatalysis under strong adsorption conditions for anions. Experimental details are provided in Online Supplementary Materials.

Voltammograms for Pt in diluted metatungstate solutions were studied earlier,[12] while comparison with more concentrated solution is shown in Figure 1. The first H UPD (underpotential deposition) peak (Figure 1, at 0.10–0.15 V) is less affected by adsorption of supporting sulfate anions, suppressed in the presence of metatungstate, and almost disappears at higher metatungstate concentration. The second peak (at > 0.20 V) is splitted and broadened with appearance of a shoulder at more

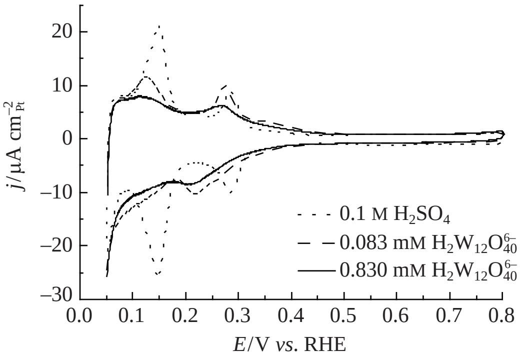


**Figure 1** Cyclic voltammograms of smooth polycrystalline Pt in 0.10 M $H_2SO_4$ and in the same solution with $(NH_4)_6H_2W_{12}O_{40}$ additives at $v$ = 10 mV s$^{-1}$, 25 °C. The data from previous work[12] was used for plotting [for 0.083 mM $(NH_4)_6H_2W_{12}O_{40}$-containing solution].

positive potentials. Qualitatively similar suppression of H UPD peaks is known for isostructural Keggin heteropoly anions,[19–21] however their effect is less pronounced even at higher concentrations. The metatungstate adsorption does not occur at potentials above 0.50 V (so-called ‘double layer’ region).

Taking into account the reported detailed analysis,[21,22] we propose a partial, but not completely irreversible, adsorption of Keggin anions on Pt. Two specific features were found earlier for adlayers of Keggin heteropoly anions: (i) the adsorbed species demonstrated $W^{VI}/W^{V}$ redox transition at more positive potentials than corresponding thermodynamic potential [‘molecular underpotential deposition (UPD)’, by analogy with UPD of metals];[21] (ii) Keggin adlayers were permeable for low-molecular species, *e.g*. did not prevent the formation of metal adatoms even at high surface coverage with large polytungstate anions.[22] For metatungstate, feature (i) was less pronounced than for Keggin heteropolyanions due to a more negative $W^{VI}/W^{V}$ equilibrium potential, *i.e.* ‘molecular UPD’ contribution to the total charge was lower. Simultaneously, metatungstate stronger suppressed H UPD as compared to heteropolyanions, especially at a higher concentration. Due to these features, the decrease of the total charge in the H UPD region (as compared to pure Pt) is stronger. At the first look, this is exactly what is needed to prevent inhibition of nitrate reduction in the case when nitrate adsorption is not suppressed to higher extent than hydrogen adsorption.

Current transients of nitrate electroreduction (Figure 2) demonstrate a decrease of reaction rate during initial period of 20–30 s, with subsequent current stabilization. The stabilization is faster than that without metatungstate (Figure S5 shows the data for 0.10 M $NaNO_3$ + 0.10 M $H_2SO_4$ solution), which indicates the less pronounced self-inhibition. The stabilization of current on platinized platinum is known[3] to require up to 1800 s, and the current decreases monotonously, similarly to our Pt foil (see Figure S5).

The most surprising qualitative effect of dissolved metatungstate was observed at potentials below 0.10 V: after initial decreasing, the current started to increase, and the steady-state (within the accuracy of 1% per minute) value was achieved only after several hours. In contrast, the behavior of Pt/$WO_x$ (Figure S6) was qualitatively analogous to that of non-modified platinum in the tungstate-free solution.

Quasi-stationary polarization curves (Figure 3) were obtained by a subtraction of currents recorded for blank experiments (in nitrate-free solutions, Figures S1–S4) from currents recorded for nitrate solutions.

The electrocatalytic effect is detected at potentials below 0.100–0.125 V in experiments with metatungstate containing solutions, whereas it is not observed for irreversibly adsorbed metatungstate (see Figure 3, solid symbols and empty boxes). However, this observation does not allow one to make an immediate conclusion about mediator-type homogeneous electrocatalysis by analogy with that reported[13–18] for glassy carbon electrode. It should be also highlighted that the catalytic effect is detected at potentials far enough from potentials of any $W^{VI}/W^{V}$ redox transitions (in Figure 3 arrows indicate the transition in adlayer; transition in solution starts at negative RHE potentials).

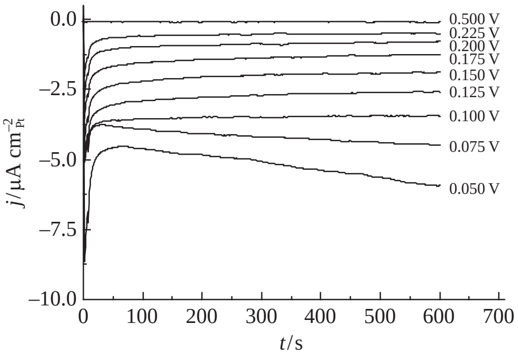


**Figure 2** Current transients for nitrate electroreduction on metatungstate-modified platinum in the 0.10 M $NaNO_3$ + 0.10 M $H_2SO_4$ + 0.83 mM $(NH_4)_6H_2W_{12}O_{40}$ solution.

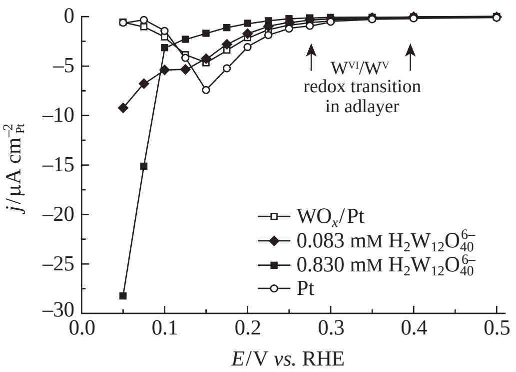


**Figure 3** Quasi-stationary polarization curves of nitrate electroreduction on smooth polycrystalline Pt measured in 0.10 M $NaNO_3$ + 0.10 M $H_2SO_4$ and with added $(NH_4)_6H_2W_{12}O_{40}$. The data from previous work[12] was used for plotting [for 0.083 mM $(NH_4)_6H_2W_{12}O_{40}$-containing solution].

For all the metatungstate-based systems in the oxygen adsorption region in the presence of nitrate, the voltammetric behavior (Figure 4) was qualitatively similar to that of previously reported[3,6] non-modified Pt. The oxygen adsorption was suppressed by nitrate in 0.80–1.0 V interval; the current observed at potentials above 1.0 V appeared to be higher than that in background solution. There is no charge balance for anodic and cathodic branches in the oxygen adsorption region, which may be related to an oxidation of N-containing adsorbate (formed in the ‘double layer’ region and sometimes interpreted as adsorbed NO). Such observations demonstrate that the reaction layers for both non-modified Pt and in the presence of metatungstate are qualitatively similar, and the adsorption-related mechanism occurs also in tungstate-containing systems. Moreover, the quantity of N-containing adsorbate is only slightly decreased in the presence of metatungstate.

The important difference between metatungstate-modified and non-modified Pt can be revealed at potentials below 0.50 V. In the presence of nitrate, the hydrogen adsorption is completely suppressed (which indicates the formation of strongly bonded N-containing adsorbate). In contrast, when the solution contains both nitrate and metatungstate, the anodic peak is clearly visible in the typical region of $W^{VI}/W^{V}$ interfacial redox transition. However, this immobilized redox couple seemingly does not play mediator role since the nitrate reduction is slower than that on non-modified Pt (see the empty symbols in Figure 3).

Considering the data shown in Figures 3 and 4, we can conclude that metatungstate behaves mostly as a ‘third body’: it occupies some centers of hydrogen adsorption at potentials below 0.10 V and simultaneously leaves enough space for the adsorption of nitrate between the edges of large adsorbed polyanions. This makes the ratio between reactants (hydrogen adatoms and N-containing adsorbates) more balanced as compared to the reaction layer on non-modified Pt (with excess of hydrogen at low potentials). We cannot also exclude some suppression of sulfate adsorption, which is known as a nitrate reduction inhibitor. However, sulfate plays a minor role in the region of low potentials, where the metatungstate effect is the most pronounced.

The presence of metatungstate in solution is important to maintain the stability of metatungstate adlayer, which contains more or less reversibly adsorbed polyanions. The metatungstate concentration is responsible for a regulation of the degree of

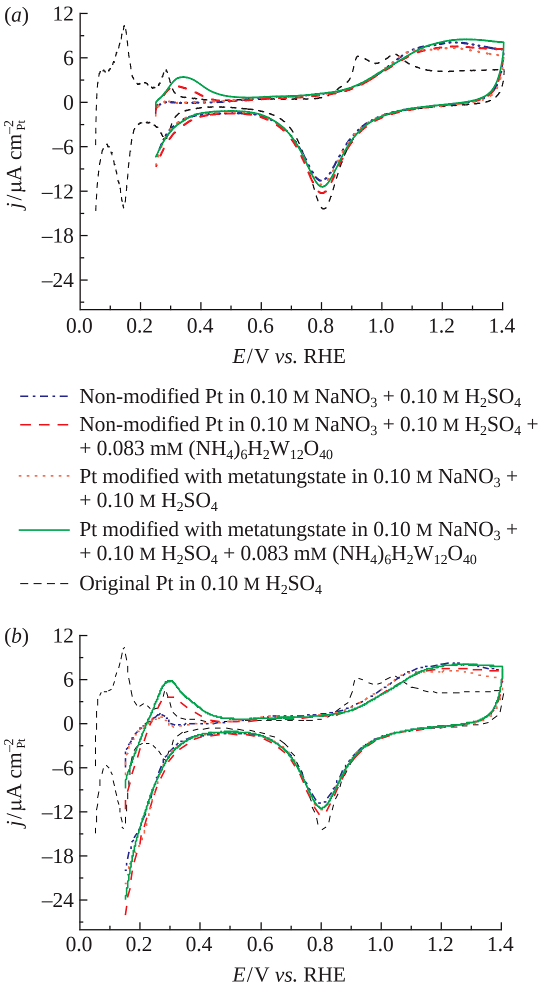


**Figure 4** The voltammograms recorded 10 min after the polarization at (*a*) 0.25 and (*b*) 0.15 V ($v$ = 5 mV s$^{-1}$, 25 °C).

hydrogen adsorption suppression. The alternative way of surface modification (*i.e*., formation of irreversibly bonded $WO_x$) results in the loss of adlayer permeability, which blocks the access of nitrate reactant to the electrode surface.

The possibility of interfacial redox mediator step in the nitrate reduction requires a further investigation. For example, some layered structures based on Ag colloid particles and substituted heteropolytungstates have been already proposed[23] and the nitrate reduction at potentials below 0.15 V RHE at pH 4.5 has been demonstrated. The hydrogenation in adlayer was completely excluded for that system, so the mediating interfacial step could be a reasonable explanation of electrocatalysis, however there were no steady-state data available at that time.

The stable steady-state current during nitrate reduction at the positive RHE potentials in the presence of metatungstate allows us to supplement the cation-based systems for nitrate electrocatalysis, being of interest for nitrate sensors. Less pragmatically, the reported results make the impact on a general electrochemistry of polyoxometallates and a future development of molecular modified electrodes. The nature of nitrate electrocatalysis is completely different in case of metatungstate and heteropolyanions studied earlier[13–18] since the latter species worked only at potentials below zero RHE.

The metatungstate anion favors nitrate reduction, while other specifically adsorbed anions inhibit it. The possible reason for such anomalous behavior is a nature of the polytungstate adlayers stabilized by strong lateral interactions due to coadsorption of cations and/or protons,[21] with weaker interaction with support. We assume that these properties, in combination with permeability for small species, can be favorable for various electrode processes.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.05.008.

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