Mathematical model for microbial fuel cells with anodic biofilms and anaerobic digestion

C. Picioreanu, K. P. Katuri, I. M. Head, M. C. M. van Loosdrecht and K. Scott

ABSTRACT

This study describes the integration of IWA's anaerobic digestion model (ADM1) within a computational model of microbial fuel cells (MFCs). Several populations of methanogenic and electroactive microorganisms coexist suspended in the anolyte and in the biofilm attached to the anode. A number of biological, chemical and electrochemical reactions occur in the bulk liquid, in the biofilm and at the electrode surface, involving glucose, organic acids, H_2 and redox mediators. Model output includes the evolution in time of important measurable MFC parameters (current production, consumption of substrates, suspended and attached biomass growth). Two- and three-dimensional model simulations reveal the importance of current and biomass heterogeneous distribution over the planar anode surface. Voltage- and power–current characteristics can be calculated at different moments in time to evaluate the limiting regime in which the MFC operates. Finally, model simulations are compared with experimental results showing that, in a batch MFC, smaller electrical resistance of the circuit leads to selection of electroactive bacteria. Higher coulombic yields are so obtained because electrons from substrate are transferred to anode rather than following the methanogenesis pathway. In addition to higher currents, faster COD consumption rates are so achieved. The potential of this general modelling framework is in the understanding and design of more complex cases of wastewater-fed microbial fuel cells.

Key words | anaerobic digestion, biofilm, mathematical model, mediator, microbial fuel cell

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INTRODUCTION

Microbial fuel cells (MFC) can directly convert mixed organic substrates to electricity using bacteria as a biocatalyst. The interest in MFC is increasing also because of suggested possibilities for effective wastewater polishing. In MFC, the biocatalytic process performed by the microorganisms differs from the natural situation because the electron flow goes to a solid electrode (e.g., anode) instead of to a natural electron acceptor (Rabaey *et al.* 2005). Although substantial knowledge already exists from traditional chemical fuel cells on mass transfer, reactions and electrical phenomena, the exact mechanisms for electron transfer from cells to electrode and the microbiology of MFCs are less well understood. Most MFC studies are still experimental, and focus either on a detailed understanding of the microbiology of bacteria involved in MFC or on engineering aspects with reports of incremental increases in performance from MFCs with increasingly advanced designs. A suitable approach to integrate information gathered from several disciplines and by researchers with backgrounds ranging from biology to engineering is by mathematical modelling. Surprisingly however, with the exception of one case from more than a decade ago (Zhang & Halme 1995) no further modelling studies have been dedicated to microbial fuel cells until very recently. In Picioreanu *et al.* (2007) we developed a general model describing the MFC behaviour with both suspended and

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attached cells in the form of biofilms. Since this was the first attempt of its kind, we studied only the electron transfer from microbial cells to the anode via a diffusible mediator, because these are compounds available in natural environments (e.g., humic acids, phenazines, quinones). In addition, it has been found that some bacteria from a biofilm enriched in an MFC can produce soluble compounds that intermediate the transfer of electrons between microorganisms and electrode (Rabaey *et al.* 2004). Including other electron transfer mechanisms in the model framework is possible, such as by cells connection to the anode via proposed conducting structures termed "nano-wires" (Reguera *et al.* 2005). In this study we aim to describe in detail only the dynamic behaviour of the anodic compartment, having in mind that a description of the cathodic chamber can follow the same approach. The anodic compartment is operated under anaerobic conditions because oxygen is usually a more efficient oxidant than the anode, competing with the desired electrochemical process. Hence, this report presents results of the integration of IWA's anaerobic digestion model (ADM1, Batstone *et al.* 2002) in the MFC model.

MODEL DEVELOPMENT

The main goal of any mathematical model of a microbial fuel cell is to, at least, calculate the electrical current and voltage generated under different operational conditions. For this, a key assumption is the mechanism by which the electrons contained in the biodegradable substrates are transferred to the solid electrode. The model developed here assumes that a redox chemical compound (electron transfer mediator, ETM) in the oxidized state acts as electron acceptor for a microbial cell using the organic substrate as electron donor. The reduced mediator is re-oxidized in an electrochemical reaction at the anode. The MFC model must so integrate in mass balances for soluble and biomass components knowledge from several areas: the electrochemical reactions on the anode surface, the biochemical reactions in the suspended and biofilm cells, the transport mechanisms for soluble components and for microbial cells. A potential balance must also be formulated, as the

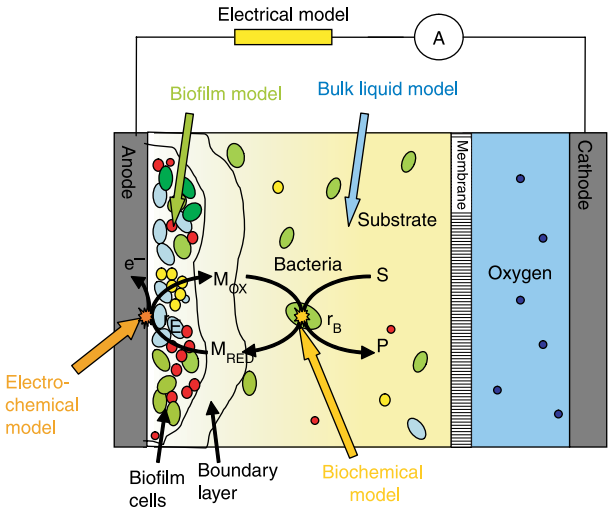

Figure 1 | The computational model for the anode compartment of the MFC comprises several sub-models for the: electrochemical reactions with redox mediator on the anode; biochemical reactions of methanogenic and electroactive microbial communities; biofilm formation; mass transport and reactions in biofilm and bulk liquid.

electrons will flow from low to high electrical potential. These sub-models are schematically shown in Figure 1. Because part of the model derivation has been recently described in Picioreanu *et al.* (2007), only the main ideas and new assumptions will be briefly presented in the following.

Electrochemical and electrical model

The current produced I [A] is calculated by integration of space-dependent current densities i [A/m^2] over the anode surface A_E [m^2]. The rate of electrochemical reaction oxidizing the ETM at the anode r_E [kmol/m^{2}s] is proportional with the current density, represented by a Butler–Volmer equation. The current density depends on the concentrations of the electroactive chemical species at the anode surface S_E [kmol/m^3] and on the activation overpotential (both function of time and location on the anode), and on reaction coefficients like exchange current density i_0 [A/m^2], Tafel slopes b[V] and number of electrons/protons involved, n. From a potential balance, the activation overpotential can be expressed function of the redox potentials of anodic (mediator oxidation) and cathodic (e.g., oxygen reduction) reactions (with values E_A

and E_C [V] corrected for concentrations at the electrode) and of ohmic overpotential. The latter sums all external and internal electrical resistances R [Ω] multiplied by the current I through the circuit. It is therefore apparent that an implicit non-linear integral–differential equation must be solved to find the current produced at each moment in time.

Biochemical model

Coupled to the electrochemical reactions, a series of biochemical reactions involving the biocatalyst (microbial cells) occur both in suspended and in attached biofilm cells. Because the MFC model aims at representing an anaerobic anode system involving a microbial community taken from an anaerobic wastewater treatment process, the biochemical model is based on the IWA's ADM1. Glucose acidification to short-chain carboxylic acids (butyric, propionic) is followed by acetate production and then by methanogenesis, including the hydrogen conversion. In addition, we assume that an electroactive microbial community (X_{eab}) can oxidize the acetate with the mediator as electron acceptor, and so participate in the current production. The reaction scheme is presented in Figure 2. The kinetic (maximum specific growth rates μ_m [1/s], saturation K_S [kmol/m^3] and inhibition K_I coefficients) and stoichiometric (yields [gCOD substrate/gCOD biomass]) parameters for acidogenesis, acetogenesis and methanogenesis are taken from ADM1 (Batstone *et al.* 2002), whereas those for the electroactive bacteria are estimated from thermodynamic considerations (as explained in Picioreanu *et al.* (2007) based on Heijnen (1999)).

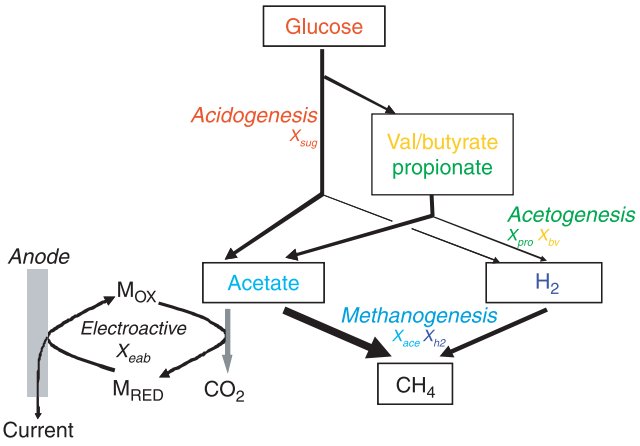

Figure 2 | The biochemical model is based on the IWA's anaerobic digestion model (ADM1) supplemented with the acetate oxidation with the electron-transfer mediator. See http://www.biofilms.bt.tudelft.nl/MFCmodelADM/index.html for parameter values, model equations and solution algorithms.

Biofilm model

Solutes

Concentrations of mediator and other soluble chemical components at the electrode surface S_E [kmol/m^3 or g COD/m^3] are determined by the transport and reaction processes occurring in the biofilm developed on the anode. The system of partial differential equations that balance diffusion and reaction rates in the biofilm is solved in either one-, two- or three-dimensional setups to find the spatial distribution of solutes in the biofilm (S_F). One boundary condition involves the bulk liquid concentrations (S_B) changed by the diffusion resistance through a mass transfer boundary layer (thickness L_L [m] and diffusivity D [m^2/s]). At the electrode surface the boundary condition equates the surface-based electrochemical reaction rate r_E with the normal component of the diffusion flux.

Biomass

An individual-based biofilm model is used to follow the dynamics of spatial distribution of different microbial populations. This includes growth and division of biomass particles determined by the local substrate concentrations, followed by biomass transport by an empirical shoving algorithm (see Picioreanu *et al.* 2007 and references within). Biomass exchange between the biofilm and suspended phases (i.e., attachment and detachment) are also included as in Xavier *et al.* (2005).

Bulk liquid model

Finally, a set of mass balances determines the time dependency of solute concentrations S_B [kmol/m^3 or gCOD/m^3] and suspended biomass X_B [gCOD/m^3] in the completely mixed bulk liquid. In the examples presented here, batch operation is simulated. Alternatively, the bulk

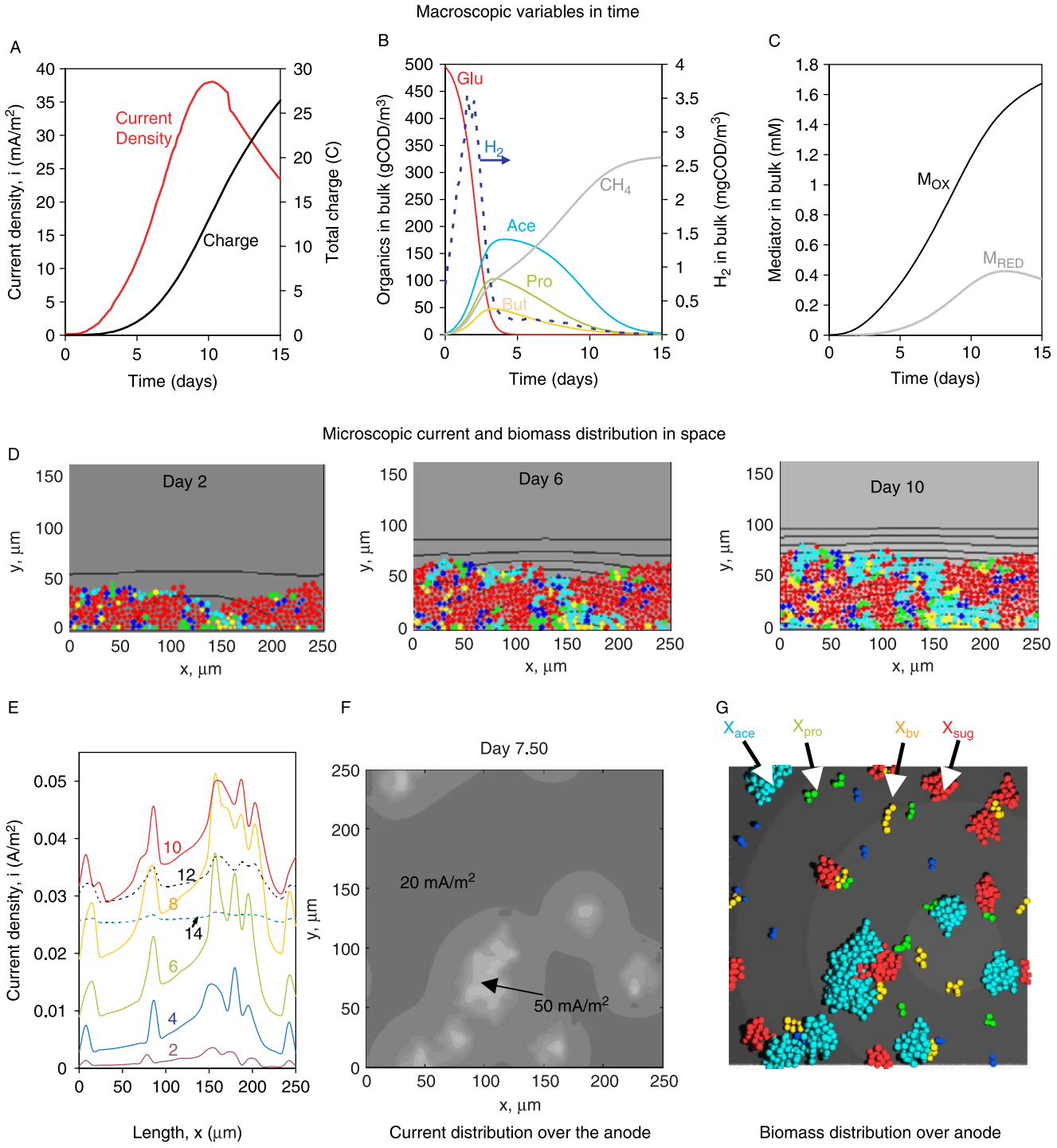

Figure 3 | Typical simulation results obtained with the 2-d (A–E) and 3-d (F–G) MFC biofilm model. (A) Current and total charge generated in time; (B) Solute concentrations in the bulk liquid; (C) Oxidized and reduced mediator in the bulk liquid; (D) Spatial distribution of microbial populations in the biofilm (consumers of: glucose X_{glu} -red-, butyrate/valerate X_{bv} -yellow-, propionate X_{pro} -green-, acetate X_{ace} -light blue-, hydrogen X_{h2} -blue-). 2-d spatial distribution of oxidized mediator is shown with iso-concentration lines and grey shades (dark grey: low-, light grey: high-concentration); (E) Current density distribution over anode at different moments in time (numbers indicate days); (F) Current density distribution over anode (dark low-, light high-current density); (G) Distribution of microbial populations on the anode (same colours as in panel D). Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst.

liquid compartment with volume V_B [m^3] can also be continuously fed with a solution containing a number of soluble substrates with the flowrate Q [m^3/s].

RESULTS

Integration of ADM and EAB

Model simulations have been performed with both added (exogenous) mediator and with internally produced (endogenous) mediator starting with an anaerobic digestion microbial community. Values of model parameters used in these simulations are from ADM1 (Batstone *et al.* 2002) and from Picioreanu *et al.* (2007). The model describes the increased current production during the biomass accumulation, with the expected fall after substrate depletion (Figure 3A). Bulk concentrations of chemical compounds follow the typically measurable trends, with glucose being quickly consumed and organic acids first generated, then utilized (Figure 3B). The slow mediator diffusion through the biofilm retards the rate of current decrease at the anode after the acetate depletion. As shown in Picioreanu *et al.* (2007), an inefficient electron transfer between cells and anode (e.g., at low mediator concentration or at low mediator potential) lets the acetate be converted both by methanogens and by electroactive bacteria (EAB), which explains why both methane and current are produced in this simulation. Older biofilms are enriched in acetate-using electroactive bacteria (Figure 3D). Unlike in the methanogenic granules used for anaerobic digestion of wastewater, the close co-location of acetogens and methanogens predicted by the model of Batstone *et al.* (2006) is not observed here. Another interesting model result is the non-uniform current density over the anode surface, due to the heterogeneous microbial distribution in the biofilm: higher currents are produced under the acetate-consuming bacteria (Figure 3E). Non-uniform current distribution occurs also when a patchy biofilm colonizes the anode, leaving large electrode areas uncovered with biomass (Figure 3F,G).

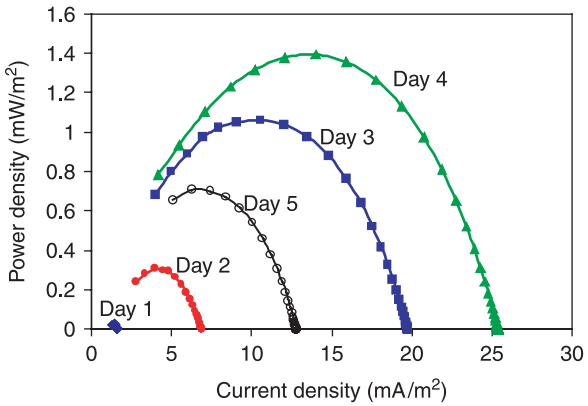

Figure 4 | Simulated power-current behaviour at different moments in time (days 1 to 5) for the MFC with electroactive microbial community in competition with the methanogens (ADM). Each curve is calculated by solving the mass balances for solutes and the total current equation at different resistances, varied from high to low values (2d model).

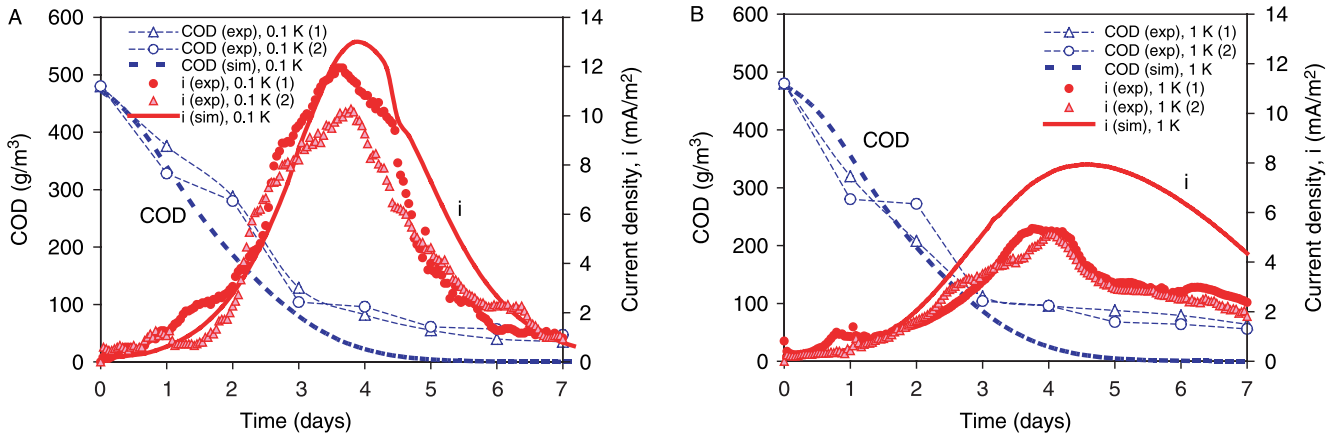

Figure 5 | Effect of the electrical resistance in the external circuit (A—100 Ω; B—1000 Ω) on the current production and COD removal. Measured current density (filled red triangles and circles) and COD (empty blue triangles and circles) are shown for duplicate experiments. The current density and COD evolution in time calculated by the model are shown with red (continuous) and blue (dashed) lines, respectively. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure http://www.iwaponline.com/wst.

In these cases, the use of 2-d or 3-d models may be justified over 1-d models, although the latter allows quicker computations and it would be recommended for flat and homogenous biofilm instances.

With the present model voltage–current and power–current characteristics for the MFC can be calculated at different moments in time. It is clear that as long as substrates are available the electroactive biomass accumulates and the power generation increases (Figure 4). Later, the diffusion limitations increase by the day, as the biofilms get thicker (Figure 3D). These model outputs are very similar to the characteristic voltage–current and voltage–power relationships observed in real MFC experiments (e.g., Logan *et al.* 2006).

Effect of external resistance on EAB selection

It is expected that the operation of MFCs at higher external resistances (ohmic loads) will limit the current allowed to flow through the circuit. Therefore, the electrode reaction coupled with the energy generation in the electroactive bacteria (EAB) will occur at a slower rate, leading not only to less current but also to less EAB in the biofilm. At the limit, in the open circuit no current flows and the EAB cannot grow (only the anaerobic digestion community develops), while the short-circuited MFC would best enrich the EAB in the biofilm. MFC experiments described elsewhere (Katuri *et al.* 2007 submitted) confirmed that indeed, the smaller the electrical resistance in the circuit, the higher the coulombic yields obtained because more of the electrons from substrate are converted into current by the larger populations of EAB. In addition to higher currents, faster COD consumption rates are achieved. These trends, as shown in Figure 5, are at least qualitatively well described by the model including the competition between the anaerobic digestion community and the electroactive bacteria.

CONCLUSIONS

This study shows how a computational model can help understand the interactions between coexisting methanogenic communities and electroactive bacteria transferring electrons to a microbial fuel cell anode via soluble redox mediators. Time dependency of MFC parameters such as current production, consumption of substrates, and production of suspended and attached biomass can be realistically computed. Model simulations are now beginning to be quantitatively compared to experimental results. It can be so explained how the anodic microbial community is enriched in electroactive bacteria at smaller resistance of the electrical circuit (i.e., when more current is let flow). Higher coulombic yields are achieved because electrons from substrate are converted into current rather than following a methanogenic path. The potential of this general modelling framework is in the understanding and design of more complex cases of wastewater-fed microbial fuel cells.

Model parameters, additional data and animations of simulated biofilm development over time can be obtained from: http://www.biofilms.bt.tudelft.nl/MFCmodelADM/index.html

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