

Electrochemical reduction of 7,7,8,8-tetracyanoquinodimethane at the n-octyl pyrrolidone/water/electrode three-phase junction

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Abstract

In this work, we investigate the applicability of TCNQ (7,7,8,8-tetracyanoquinodimethane) for cation transfer at a three-phase electrode. This molecule is a noted organic redox probe for studies of heterogeneous electron transfer at the interface of two immiscible electrolyte solutions. Although it was also recently proposed as a potential candidate for cation transfer studies at a three-phase junction [S. Wu, B. Su, J. Electroanal. Chem. 656 (2011) 237–242] our results clearly show that its reduced form is not sufficiently hydrophobic for this particular application. Expulsion of the redox probe was confirmed by both the decrease of current for consecutive scans, as well as lack of dependence of the peak potential on the type of cation present in the aqueous phase. Anion dependence of the peak potential as well as differences in behaviour observed for inorganic and organic cations present in the aqueous solution further confirm that TCNQ is not a suitable candidate for cation transfer studies at the three-phase junction.

Keywords: TCNQ, three-phase junction, 7,7,8,8-tetracyanoquinodimethane, n-octyl pyrrolidone/water interface, ITIES, two-phase electrochemistry

1. Introduction

TCNQ (7,7,8,8-tetracyanoquinodimethane) is a redox active organic molecule, which can undergo a two-step one-electron reversible reduction via the radical anion (TCNQ^{•-}) to the dianion (TCNQ²⁻) in acetonitrile and 1,2-dichloroethane [1–7]. The electrochemical generation of TCNQ^{•-} in acetonitrile having different transition metal electrolytes (Cu, Co, Ni, Zn, Cd, Ag, and Mn) is a common way to prepare semiconducting metal-TCNQ complexes [7,8]. Applications of such compounds, ranging from data storage to sensing and catalysis together with their synthetic routes, were recently reviewed by Alan Bond's group [9]. Moreover, TCNQ is well-known to form highly conductive charge-transfer complexes with different metals due to its strong electron acceptor property (electron affinity 2.88 eV) and delocalised electronic structure. Both reduced forms TCNQ^{•-} and TCNQ²⁻ are excellent ligands for the synthesis of coordination polymers and metalorganic frameworks [9]. TCNQ is insoluble in water, hence reduction on a TCNQ modified glassy carbon (GC) electrodes in transition metal aqueous solutions leads to the deposition of metal-TCNQ coordination polymers [9,10].

Various metal-TCNQ complexes have found applications in electron transfer reactions, galvanic replacement reactions for photocatalytic degradation of organic dyes and catalysis [11]. Metal-free TCNQ and its derivatives are suggested as low-cost high-capacity, monomeric organic cathode materials for lithium-ion batteries, which are expected to possess high cell voltage [6,12–14]. Additionally, a derivative of TCNQ and 11,11,12,12-tetracyano-9,10-anthraquinodimethane gained substantial interest in many fields such as light-emitting diodes, photoinduced electron transfer, molecular rectifiers, organic optoelectronic devices, sensors and field effect transistors [15–17].

In acetonitrile, two reversible one-electron reductions of TCNQ are diffusion controlled. The diffusion coefficient for both TCNQ and $\text{TCNQ}^{\cdot-}$ is nearly the same (1.9 and $1.7 \text{ cm}^2 \text{ s}^{-1}$ respectively) but considerably larger than for the TCNQ^{2-} ($1.2 \text{ cm}^2 \text{ s}^{-1}$) [5]. $\text{TCNQ}^{\cdot-}$ is quite stable under ambient condition [9] whereas TCNQ^{2-} decomposes to dicyano-p-toluoylcyanide in the presence of oxygen [5,18,19]. The stability of TCNQ anions and the effect of acid on the chemical/electrochemical reduction of TCNQ are well studied. Yamagishi and co-workers reported the kinetics of $\text{TCNQ}^{\cdot-}$ protonation to HTCNQ^{\cdot} species in acidic aqueous and organic solvent systems (methanol, ethanol and acetonitrile in presence of HCl) [20–22]. In spite of aerial oxidation of TCNQ^{2-} , the protonation is achieved in the presence of appropriate metal cations and as shown by Robson et al [23,24] it is possible to obtain air-stable H_2TCNQ . This approach was used further to produce various metal(II)-TCNQ coordination polymers [24]. Also, electrochemical reduction of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF_4) in acetonitrile makes it possible to generate an air-stable TCNQF_4^{2-} dianion [15]. Ion pair formation between (electrochemically generated) TCNQ^{2-} with different mono- and bivalent cations is well studied in acetonitrile and DMSO [25–27]. It was shown that cations of +2 charge, like Ba^{2+} and Mg^{2+} showed stronger ion-pair interactions than alkaline metals of +1 charge, such as Na^+ [27].

Although TCNQ is insoluble in water it is possible to study its interactions with aqueous electrolytes by means of liquid/liquid electrochemistry. In situ generated $\text{TCNQ}^{\cdot-}$ was used to study the electron transfer rate between the reduced compound and a redox probe across the liquid-liquid interface using scanning electrochemical microscopy [28,29]. It was shown that the electron transfer was accompanied by the transfer of anions from the aqueous phase in case of 1,2-dichloroethane and by the expulsion of the $\text{TCNQ}^{\cdot-}$ when nitrobenzene was used as the organic phase [29].

TCNQ can form metal-TCNQ compounds as metal ions are transferred across the liquid/liquid interface [3]. A study by Wu and Su [4] showed that reduction of TCNQ at a three-phase junction between water, 2-nitrophenyl octyl ether and a screen-printed carbon electrode can lead to the transfer of cations from the aqueous to the organic phase. This is quite uncommon since expulsion of reduced probe from the organic to aqueous phase is the most probable reaction pathway when a neutral compound is reduced at the three-phase electrode (TPE configuration) [30,31]. Although many organic compounds are insoluble in water, their salts formed by reduction and association with a cation are often quite soluble. Studies of microcrystals of TCNQ immobilised on electrodes in aqueous electrolytes with alkali ions show that the alkali cations readily form salts with the $\text{TCNQ}^{\bullet-}$ [1,32,33]. The highest solubility is observed for the $\text{Li}^+ \text{TCNQ}^{\bullet-}$, whereas the higher alkali salts, as well as those formed with bivalent cations are much less soluble [32]. Due to these intriguing results observed at the screen-printed electrode, in this article, we decided to investigate the electrochemistry of TCNQ at a standard droplet-based TPE in a water/NOP system. This study is intended to shed some light on the applicability of TCNQ as a redox probe for cation transfer studies.

2. Experimental

7,7,8,8-tetracyanoquinodimethane (TCNQ) (Sigma-Aldrich), n-octyl-2-pyrrolidone (NOP, Santa Cruz Biotechnology) and 2-nitrophenyl octyl ether (NPOE, Sigma-Aldrich) were used as received without further purification. All the inorganic salts were dissolved in ultrapure water to prepare the aqueous phase, which was not saturated with NOP or NPOE solvents.

All the experiments were performed using a SP-300 Biologic or PalmSens4 potentiostats. Preliminary experiments to determine the redox behaviour of TCNQ in NOP solvent were performed after deoxygenation with argon gas. In this case, a 3-electrode cell setup with GC working, Ag wire quasi-reference and Pt counter electrodes were used. Three-phase experiments were performed in a standard three-electrode setup with a glassy carbon working (3 mm radius), Ag/AgCl (3.5 M KCl) reference and a Pt wire as the counter electrode. 10 mM TCNQ was dissolved in NOP solvent, a droplet of 2 μL -in-volume was attached on the GC and submerged in the aqueous electrolyte to create the three-phase junction (see scheme in **Fig. 1**).

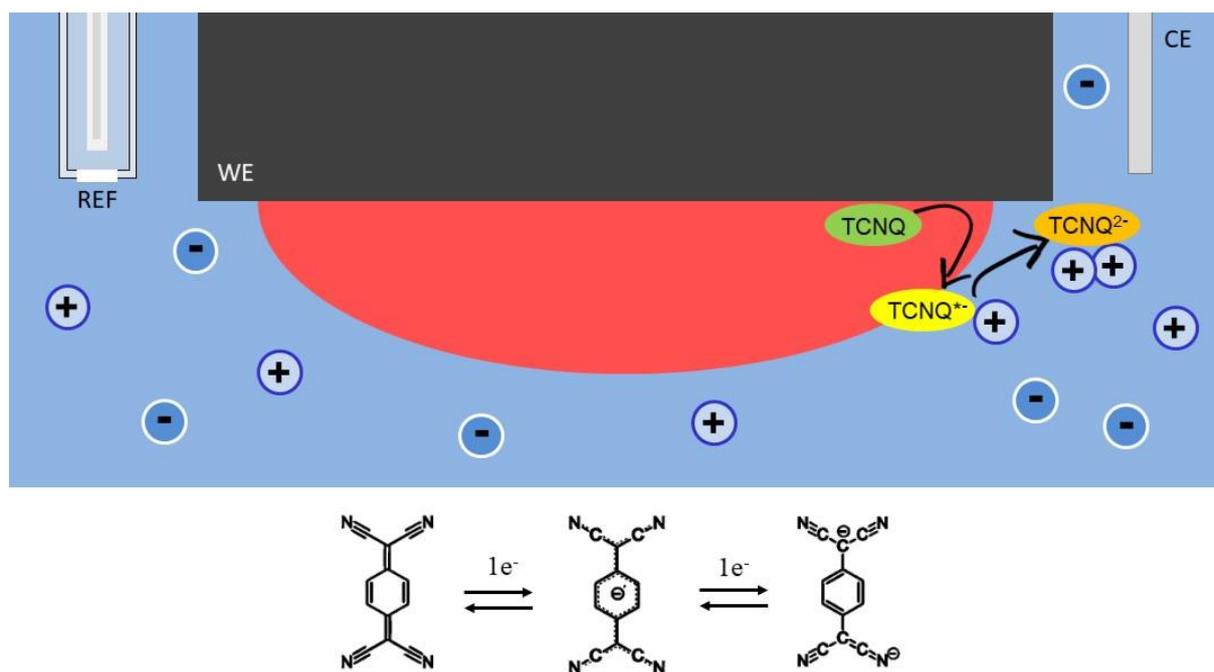


Fig. 1 Schematic illustration of the experimental setup

3. Results and discussion

Preliminary CV studies of 10 mM TCNQ in NOP solvent having 0.1 M TBAClO₄ and LiClO₄ as the supporting electrolyte are shown in **Fig. 2**. Two subsequent one-electron reductions of TCNQ to TCNQ^{•-} and TCNQ^{2•-} in NOP are observed, which is in good agreement with previous reports where CVs were performed in NPOE [4], 1,2-dichloroethane [3] and acetonitrile [1–7]. But in acetonitrile and 1,2-dichloroethane, TCNQ successive reductions are, diffusion-controlled, chemically, and electrochemically reversible. In NOP, the redox process is strongly influenced by the supporting electrolyte. As seen in **Fig. 2** in the case of LiClO₄ both reduction peaks are pronounced and reversible. However, in TBAClO₄ we can observe that the second reduction peak is poorly developed, which may be attributed to limited interaction between TCNQ^{2•-} and TBA⁺ in the quite viscous NOP solvent. The corresponding SWV is shown in **Fig. S1**.

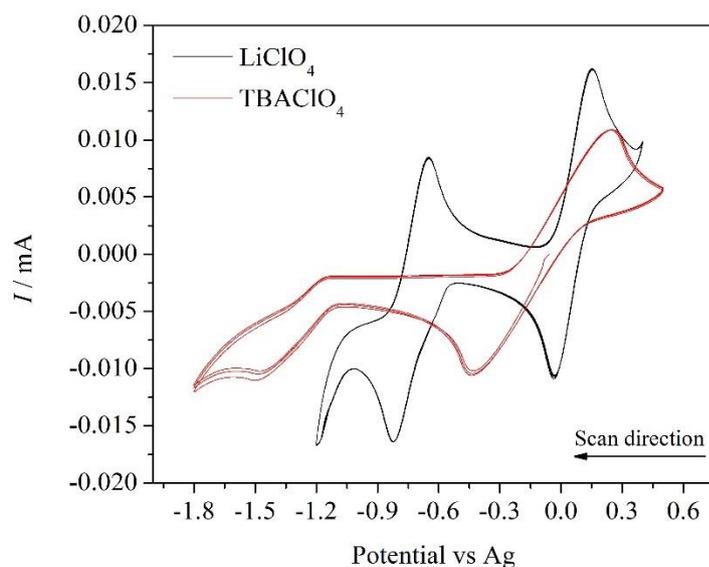
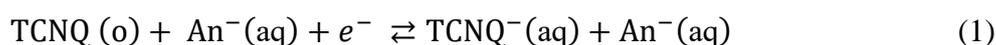


Fig. 2. CVs (50 mV s^{-1}) of 10 mM TCNQ dissolved in NOP solvent having 0.1 M TBAClO₄ or LiClO₄ supporting electrolyte.

Fig. 3 shows results from the 3-phase measurements. Multiple subsequent CV cycles of 10 mM TCNQ dissolved in NOP droplet deposited on the GC electrode and submerged in 0.1 M KNO₃ (**Fig. 3a**) aqueous solution are shown. To maintain charge neutrality of the NOP phase after the electrochemical reduction of TCNQ either transfer of the counter cations from W to NOP or the transfer of the reduced TCNQ anions (TCNQ^{•-} and TCNQ²⁻) from NOP to W phase can occur. The cation transfer takes place if the free energy of such transfer is lower than the free energy of expulsion of the reduced TCNQ anions from NOP to the W phase. The theory of ion-transfer at three-phase electrode was recently summarised by Scholz and co-workers in [30]. The marked decrease in peak currents (indicated with arrows) for the subsequent CV cycles (**Fig. 3**) indicates the expulsion of the redox probe during cycling. This is probably due to an increase in the water solubility of TCNQ upon salt formation between TCNQ anions and alkali/alkaline metal cations during the reduction at 3-phase junction. When a reducible non-ionic compound is dissolved in a nonpolar organic solvent (like NOP), expulsion of the reduced form from the organic to the water phase is the most common pathway [30]:



Similar results were obtained when the aqueous electrolyte was based on a more hydrophobic cation (TBA⁺) (**Fig. 3b**). When measured a different scan rates the decrease of the peaks is much faster during slow scans where the ions have more time to diffuse away from the liquid junction into the bulk of the aqueous phase (**Fig. S2a**). Conversely, at a high scan rate, the

decrease between subsequent scans is smaller (**Fig. S2b**). We can estimate the energy needed for the expulsion of the $\text{TCNQ}^{\cdot-}$ by comparing the experiments in NOP with the three-phase experiments. We performed cyclic voltammetry of ferrocenedimethanol in both aqueous and organic solutions of TBACl (**Fig. S3**). Assuming that the redox potential is the same in the two solutions, although in NOP the reaction is quite sluggish [34], gives a shift between the Ag|AgCl reference electrode and the Ag wire quasi-reference of 530 mV. Comparing the redox potentials for the first TCNQ redox reaction in NOP with LiClO₄ in Fig 1 and in the three-phase system (details below) we get $\Delta E = 190\text{--}360$ mV depending on the anion in the aqueous solution. This corresponds to an expulsion energy $\Delta G = 18\text{--}35$ kJ/mol, which of similar magnitude as ion-transfer potentials between water and NPOE cited by Samec et al. [35].

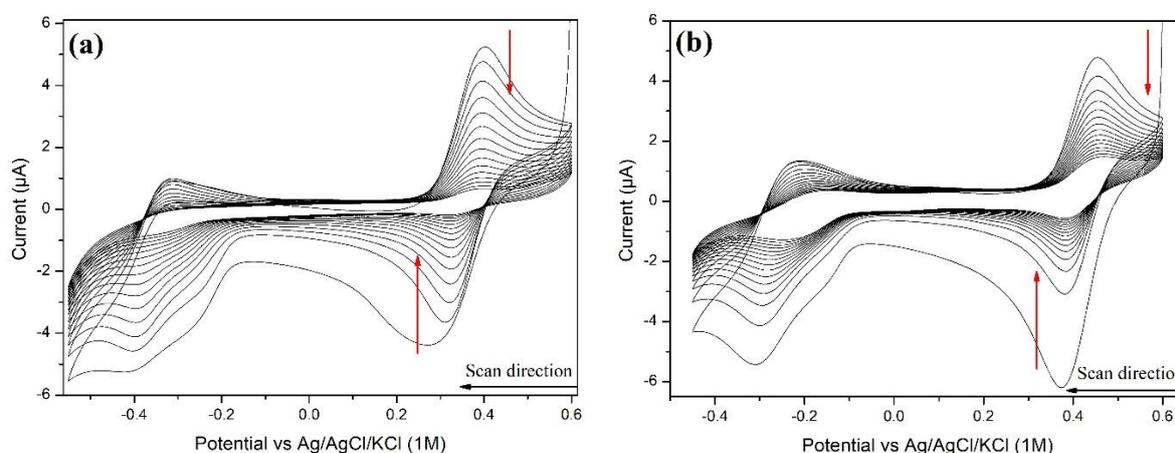


Fig. 3. (a) 15 consecutive three-phase junction CVs (20 mVs^{-1}) of the NOP droplet having 10 mM TCNQ on GC immersed in 0.1 KNO_3 and (b) in 0.1 TBACl solution

In **Fig. S4** it can be seen that the expulsion of the probe is observed also if only the first reduction is taking place. The expulsion can be limited to some extent by scanning at higher rates (100mV/s and above), not giving the anion time to diffuse away. CVs scanned to a more negative potential are shown (**Fig. S5**). Here we can see a third, irreversible, reduction peak. As described above, the first two reductions (**Fig. 3a and 3b**) are attributed to the reduction of TCNQ to $\text{TCNQ}^{\cdot-}$ and TCNQ^{2-} respectively. The third reduction may be the reduction of dicyano-*p*-toluoylcyanoide, since TCNQ^{2-} decomposes to dicyano-*p*-toluoylcyanoide due to the presence of oxygen and water in the 3-phase configuration [19,36]. It is possible that the third reduction could be associated with another species, such as the protonated TCNQ (HTCNQ^- and H_2TCNQ), although this is unlikely. Under these conditions, protonation of TCNQ^{2-} (to electroactive HTCNQ^- and electro inactive H_2TCNQ) is difficult before it decomposes to dicyano-*p*-toluoylcyanoide and only in dry box condition, the protonation of TCNQ^{2-} will

generate the electroactive HTCNQ^- . Moreover, the reduction of HTCNQ^- undergoes at a more positive potential in relation to the TCNQ^{2-} reduction [5].

Further, as shown in **Fig. 4a** and **4b**, the reduction potential for neither of the three reductions changes substantially regardless of the cation (of +1 and +2 charge) present in the aqueous electrolyte. If the reduction would be associated with cation transfer the SWV peak potentials should shift to more negative values for more hydrophilic cations ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$) as shown by Quentel et al [37] and Scholz et al [38]. However, it is well known that the reduction of TCNQ to TCNQ^{2-} in acetonitrile results in ion-pair formation with cations of +2 charge (Ba^{2+} and Mg^{2+}) [27]. In our previous work [31], the three-phase reduction of quinones was accompanied by the transfer of cations from water to NOP and the reduction potentials followed the ionic potentials of the cations (due to ion-pair formation with the transferred cations) rather than their hydrophilicity. In the case of TCNQ , as shown in **Fig. 4**, this behaviour is absent, which further indicates lack of associated cation transfer.

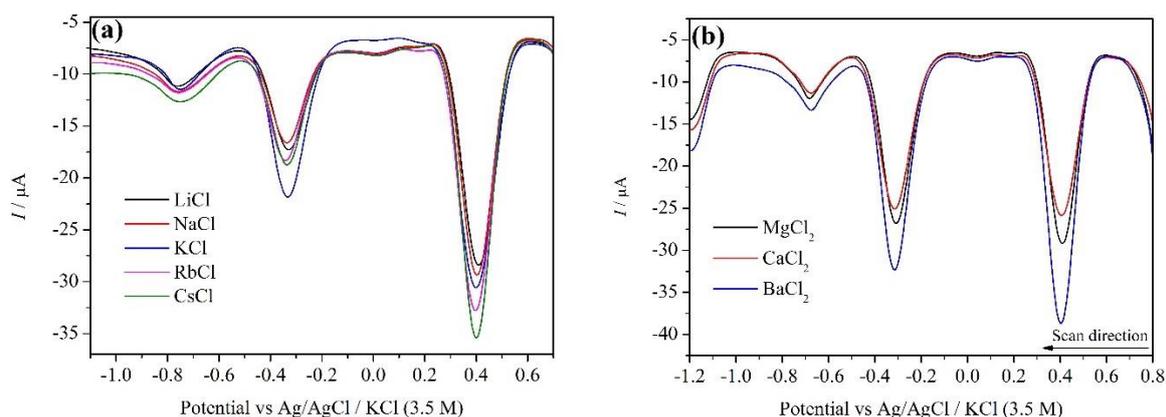


Fig. 4. SWVs of 10 mM TCNQ in NOP droplet on GC and immersed in 0.1M electrolytes of different cations of (a) +1 and (b) +2 charge.

On the other hand, we observed that the peak potential of the first reduction clearly depends on the hydrophilicity of the *anion* present in the aqueous electrolyte (**Fig. 5a**). The negative shift in the reduction potential ($\text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{SCN}^- < \text{ClO}_4^- < \text{PF}_6^-$) follows the hydrophobicity of the anions due to the salting out effect when TCNQ^- is expelled from NOP to the aqueous phase [39]. This result is identical with that presented in our recent article, where we observed the salting out effect of the 2,3-dichloro-1,4-naphthoquinone radical anion at the NOP/water interface [31]. Although the reduction peak potential follows the hydrophobicity of the anion, the relationship is not linear as would be expected in the case of ion insertion into the organic phase (see **Fig. S6**). TCNQ^- salts of alkali, alkaline earth metal, and tetraalkylammonium ions are easily formed at room temperature upon one-electron reduction

of TCNQ treated with certain metals, metal iodides, and alkyl-substituted ammonium [40,41]. The potential of the second reduction is not influenced by the type of anion, as seen in **Fig. 5b**. This is expected since the $\text{TCNQ}^{\cdot-}$ has already transferred to the aqueous phase, where further reduction takes place, and no associated ion transfer is needed. The exception is in the presence of the relatively large ions, PF_6^- and SCN^- where the second reduction occurs at less negative potential than for the other ions. A series of subsequent SWVs were recorded for the same droplet (**Fig. S7**), the decrease in current (marked with arrow) during each successive scan further indicates the expulsion of reduced TCNQ.

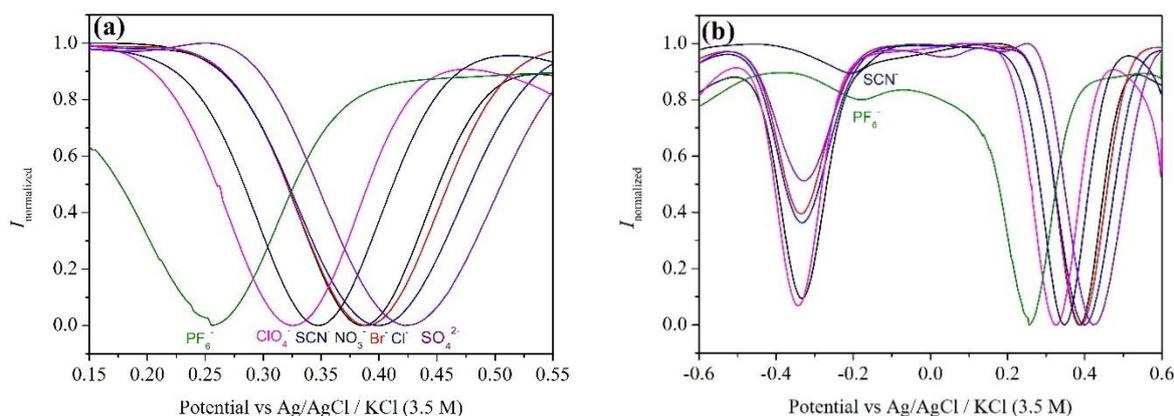


Fig. 5. SWVs of 10 mM TCNQ in NOP droplet on GC and immersed in electrolytes of different anions

When the aqueous electrolyte is based on one of the organic quaternary ammonium salts the reduction from TCNQ to $\text{TCNQ}^{\cdot-}$ is also characterized by a clear decrease of current with each successive scan. The potential of the first reduction peak is stable during consecutive measurements performed on the same droplet (**Fig. S8 a-d**). However, in the case of the second reduction, there is a clear potential shift towards more negative values for TBACl and TMAcI and towards more positive values for TPACl. The reason for this behaviour is not quite understood. The comparison of SWVs showing the first reduction of different tetralkylammonium salts is shown in **Fig. 6**, only a very small peak shift can be seen in the order of lipophilicity of the organic cations $\text{TBA}^+ < \text{TPA}^+ < \text{TEA}^+ < \text{TMA}^+$. No peak potential dependency on concentration (1 M, 0.1M, and 0.01M) of TBA cation was observed for this process (**Fig. S9**), supporting the hypothesis that the process is dominated by the expulsion of the $\text{TCNQ}^{\cdot-}$ anion. However, in a non-linear manner, concentration influences the second and third reduction peak potentials.

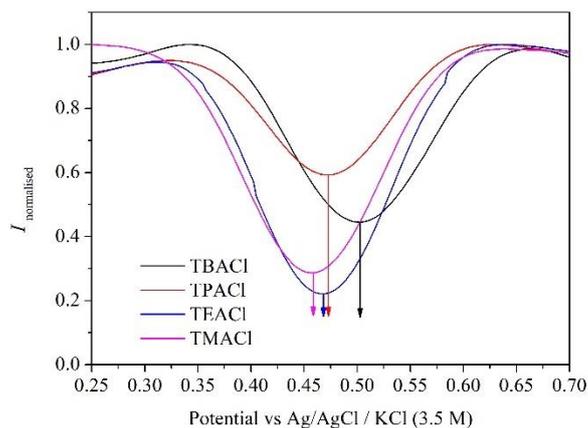


Fig. 6. SWVs of 10 mM TCNQ in NOP droplet on GC and immersed in electrolytes of different tetraalkylammonium cations

As mentioned above, it was already noted that the electrochemistry of TCNQ is highly dependent on the nature of the solvent. In case of reduced TCNQ^{•-} electron transfer can be accompanied by the anion transfer from water to the organic phase or expulsion of the redox probe depending if the reaction is carried out with 1,2-dichloroethane or nitrobenzene, respectively [29]. Given that the cation transfer using TCNQ as a redox probe in TPE configuration was previously observed using NPOE [4], electrochemistry in this solvent was also investigated (**Fig. 7**). As compared with NOP (**Fig. 2**) striking is the lack of reversibility of the second reduction step. A clear decrease in charge of about 5% with each consecutive scan is still visible even if the measurement is carried out only in the shortened potential range before the irreversible reduction can take place (**Fig. 7 inset**), which would indicate expulsion of the reduced TCNQ^{•-} as seen in the case of NOP. These data are in contrast to the results published by Wu and Su [4]. We can only speculate that some interaction with the screen-printed electrode used in their measurements influences the transfer of the TCNQ^{•-}. In any case, this would indicate that similarly as in the case of NOP, TCNQ is not a suitable redox probe for three-phase electrochemistry studies using glassy carbon electrodes.

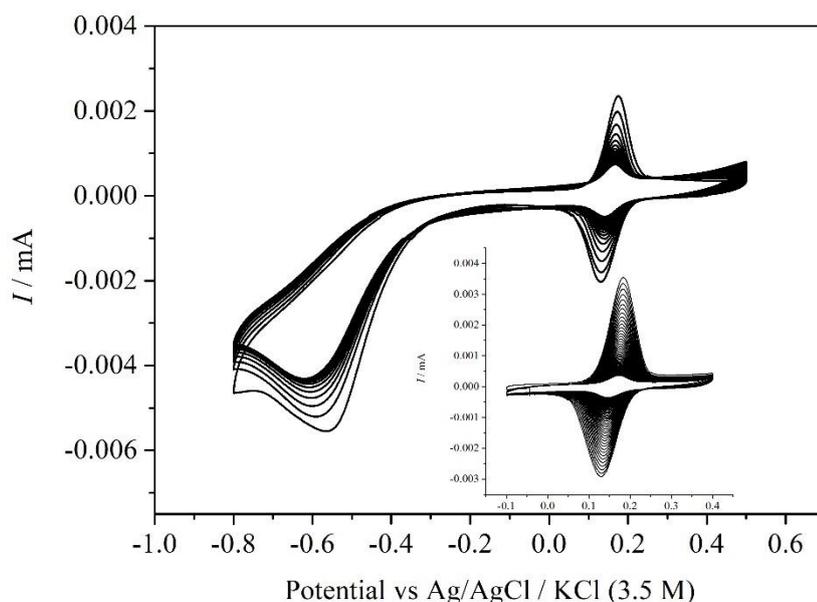


Fig. 7. 30 consecutive three-phase junction CVs (20 mVs^{-1}) of the NPOE droplet having 10 mM TCNQ on GC immersed in 0.1 TBACl solution.

Conclusions

Studies of ion transfer voltammetry at the three-phase electrode are often limited by the number of redox probes available. Although there is a considerable number of molecules which are sufficiently hydrophobic after oxidation than can serve for investigation of the anion transfer process, finding a redox probe which can be reduced and not pass to the aqueous phase is still a challenge [42]. Even though TCNQ (7,7,8,8-tetracyanoquinodimethane) is widely applied in heterogeneous electron transfer at the interface between two immiscible electrolyte solutions there are still many unknowns regarding the mechanism of its redox process in biphasic systems. More than 20 years ago, Bond and co-workers[1] showed it is possible to use this molecule for inorganic cation transfer in a thin film configuration. In 2011 it was also stipulated that TCNQ can be used for cation-coupled electron transfer in a three-phase junction setup [4]. Due to those promising reports, we decided to investigate its electrochemistry at a three-phase junction using n-octyl-2-pyrrolidone (NOP) as the organic phase. An aprotic nonpolar solvent was chosen to limit the number of possible processes, in particular, protonation of the TCNQ anions. We have shown that TCNQ is not retained in the organic phase, as the current decreases with each successive scan. We also did not observe any transfer of inorganic cations. The absence of any dependence of the reduction potential on the cation used and clear dependence on the anion hydrophobicity confirm the expulsion of the reduced TCNQ anion. Although weak dependence of the reduction potential on the concentration and lipophilicity or organic cations

was observed, the measured shift in the potential is too small to let us think that TCNQ could be used as a redox probe for cation transfer studies in this setup. Similar behaviour in a different solvent, namely 2-nitrophenyl octyl ether (NPOE) is in contrast with previous reports using a different type of working electrode. In summary, this leads us to conclude that the electrochemistry of TCNQ at a three-phase junction is too complex and dependant on too many factors to be a reliable redox probe in this kind of experiments. A more suitable system might be the thick-film setup where the limited hydrophobicity of the reduced form is less of an issue. [43]

Acknowledgements

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References

- [1] A.M. Bond, S. Fletcher, F. Marken, S.J. Shaw, P.G. Symons, Electrochemical and X-ray diffraction study of the redox cycling of nanocrystals of 7,7,8,8-tetracyanoquinodimethane. Observation of a solid–solid phase transformation controlled by nucleation and growth, *J. Chem. Soc., Faraday Trans.* 92 (1996) 3925–3933. doi:10.1039/FT9969203925.
- [2] G.N. Kamau, J.F. Rusling, Microelectrode voltammetry of TCNQ in aprotic solvent at low concentrations of non-reducing and reducing salts, *J. Electroanal. Chem.* 292 (1990) 187–198. doi:10.1016/0022-0728(90)87335-H.
- [3] L. Huang, P. Li, N. Pamphile, Z.Q. Tian, D. Zhan, Electrosynthesis of Copper-Tetracyanoquinodimethane Based on the Coupling Charge Transfer across Water/1,2-Dichloroethane Interface, *Electrochim. Acta.* 140 (2014) 332–336. doi:10.1016/j.electacta.2014.04.102.
- [4] S. Wu, B. Su, 7,7',8,8'-Tetracyanoquinodimethane as a redox probe for studying cation transfer across the water/2-nitrophenyl octyl ether interface at three-phase junctions supported by carbon ink screen-printed electrodes, *J. Electroanal. Chem.* 656 (2011) 237–242. doi:10.1016/j.jelechem.2010.11.004.
- [5] T.H. Le, A. Nafady, X. Qu, A.M. Bond, L.L. Martin, Redox and Acid–Base Chemistry of 7,7,8,8-Tetracyanoquinodimethane, 7,7,8,8-Tetracyanoquinodimethane Radical Anion, 7,7,8,8-Tetracyanoquinodimethane Dianion, and Dihydro-7,7,8,8-Tetracyanoquinodimethane in Acetonitrile, *Anal. Chem.* 84 (2012) 2343–2350. doi:10.1021/ac2030514.
- [6] Y. Kanzaki, S. Mitani, D. Shiomi, Y. Morita, T. Takui, K. Sato, Microscopic Behavior of Active Materials Inside a TCNQ-Based Lithium-Ion Rechargeable Battery by in Situ 2D ESR Measurements, *ACS Appl. Mater. Interfaces.* 10 (2018) 43631–43640. doi:10.1021/acsami.8b14967.
- [7] A.R. Harris, A.K. Neufeld, A.P. O'Mullane, A.M. Bond, R.J.S. Morrison, Voltammetric, EQCM, Spectroscopic, and Microscopic Studies on the Electrocrystallization of Semiconducting, Phase I, CuTCNQ on Carbon, Gold, and Platinum Electrodes by a Nucleation-Growth Process, *J. Electrochem. Soc.* 152 (2005) C577. doi:10.1149/1.1955047.

- [8] A. Nafady, A.M. Bond, A. Bilyk, A.R. Harris, A.I. Bhatt, A.P. O'Mullane, R. De Marco, Tuning the electrocrystallization parameters of semiconducting Co[TCNQ]₂-based materials to yield either single nanowires or crystalline thin films, *J. Am. Chem. Soc.* 129 (2007) 2369–2382. doi:10.1021/ja067219j.
- [9] A. Nafady, A.P. O'Mullane, A.M. Bond, Electrochemical and photochemical routes to semiconducting transition metal-tetracyanoquinodimethane coordination polymers, *Coord. Chem. Rev.* 268 (2014) 101–142. doi:10.1016/j.ccr.2014.01.017.
- [10] A.K. Neufeld, I. Madsen, A.M. Bond, C.F. Hogan, Phase, Morphology, and Particle Size Changes Associated with the Solid–Solid Electrochemical Interconversion of TCNQ and Semiconducting CuTCNQ (TCNQ = Tetracyanoquinodimethane), *Chem. Mater.* 15 (2003) 3573–3585. doi:10.1021/cm0341336.
- [11] M. Mohammadtaheri, R. Ramanathan, V. Bansal, Emerging applications of metal-TCNQ based organic semiconductor charge transfer complexes for catalysis, *Catal. Today.* 278 (2016) 319–329. doi:10.1016/j.cattod.2015.11.017.
- [12] Y. Hanyu, I. Honma, Rechargeable quasi-solid state lithium battery with organic crystalline cathode, *Sci. Rep.* 2 (2012) 1–6. doi:10.1038/srep00453.
- [13] S. Tobishima, Cathode Characteristics of Organic Electron Acceptors for Lithium Batteries, *J. Electrochem. Soc.* 131 (1984) 57. doi:10.1149/1.2115542.
- [14] S. Nishida, Y. Yamamoto, T. Takui, Y. Morita, Organic Rechargeable Batteries with Tailored Voltage and Cycle Performance, *ChemSusChem.* 6 (2013) 794–797. doi:10.1002/cssc.201300010.
- [15] T.H. Le, A. Nafady, X. Qu, L.L. Martin, A.M. Bond, Detailed Electrochemical Analysis of the Redox Chemistry of Tetrafluorotetracyanoquinodimethane TCNQF 4, the Radical Anion [TCNQF 4]^{•-}, and the Dianion [TCNQF 4]²⁻ in the Presence of Trifluoroacetic Acid, *Anal. Chem.* 83 (2011) 6731–6737. doi:10.1021/ac201373d.
- [16] R. Gómez, C. Seoane, J.L. Segura, The first two decades of a versatile electron acceptor building block: 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ), *Chem. Soc. Rev.* 36 (2007) 1305–1322. doi:10.1039/b605735g.
- [17] L. Segura, C. Seoane, Design and synthesis of TCNQ and DCNQI type electron acceptor molecules as.pdf, 7 (1997) 1661–1676.
- [18] M.C. Grossel, A.J. Duke, D. Brynn Hibbert, I.K. Lewis, E.A. Seddon, P.N. Horton, S.C. Weston, An investigation of the factors that influence the decomposition of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) and its salts to, and structural characterization of, the α,α -dicyano-p-toluoylcyano anion, *Chem. Mater.* 12 (2000) 2319–2323. doi:10.1021/cm991160g.
- [19] M.R. Suchanski, R.P. Van Duyne, Resonance Raman spectroelectrochemistry. IV. The oxygen decay chemistry of the tetracyanoquinodimethane dianion, *J. Am. Chem. Soc.* 98 (1976) 250–252. doi:10.1021/ja00417a049.
- [20] A. Yamagishi, M. Sakamoto, The Protonation of the TCNQ Anion Radical by Hydrogen Chloride, *Bull. Chem. Soc. Jpn.* 47 (1974) 2152–2157. doi:10.1246/bcsj.47.2152.
- [21] Y.M. Yamagishi Akihiko, Effects of Quinones on the Protonation Reaction of TCNQ Anion Radical; The Role of a Protonated Quinone as a Strong Electron Acceptor, *Bull. Chem. Soc. Jpn.* 49 (1976) 371–374. doi:10.1246/bcsj.49.371.

- [22] A. Yamagishi, Rate of Protonation of TCNQ Anion Radical in Water, *Bull. Chem. Soc. Jpn.* 49 (1976) 1417–1418. doi:10.1246/bcsj.49.1417.
- [23] T.A. Hudson, R. Robson, A new class of TCNQ derivatives easily generated from TCNQH₂ containing discrete TCNQ²⁻ anions and noncoordinating cations, *Cryst. Growth Des.* 9 (2009) 1658–1662. doi:10.1021/cg801400j.
- [24] B.F. Abrahams, R.W. Elliott, T.A. Hudson, R. Robson, A new type of 3D [(MII)₂(TCNQ-II)₃]₂-coordination network with spacious channels of hexagonal cross-section generated from TCNQH₂, *CrystEngComm.* 14 (2012) 351–354. doi:10.1039/c1ce06104f.
- [25] S.B. Khoo, J.K. Foley, S. Pons, Electrolyte effects on the cyclic voltammetry of TCNQ and TCNE, *J. Electroanal. Chem. Interfacial Electrochem.* 215 (1986) 273–285. doi:10.1016/0022-0728(86)87021-8.
- [26] S.B. Khoo, J.F. Foley, C. Korzeniewski, S. Pons, C. Marcott, An infrared spectroelectrochemical investigation of the ion pairing reactions of the anions and dianions of TCNE and TCNQ, *J. Electroanal. Chem. Interfacial Electrochem.* 233 (1987) 223–236. doi:10.1016/0022-0728(87)85018-0.
- [27] M. Oyama, R.D. Webster, M. Suárez, F. Marken, R.G. Compton, S. Okazaki, Mechanistic Aspects of the Electrochemical Reduction of 7,7,8,8-Tetracyanoquinodimethane in the Presence of Mg²⁺ or Ba²⁺, *J. Phys. Chem. B.* 102 (1998) 6588–6595. doi:10.1021/jp9819846.
- [28] F. Li, A.L. Whitworth, P.R. Unwin, Measurement of rapid electron transfer across a liquid/liquid interface from 7,7,8,8-tetracyanoquinodimethane radical anion in 1,2-dichloroethane to aqueous tris(2,2-bipyridyl)-ruthenium (III), *J. Electroanal. Chem.* 602 (2007) 70–76. doi:10.1016/j.jelechem.2006.12.002.
- [29] J. Zhang, P.R. Unwin, Microelectrochemical measurements of electron transfer rates at the interface between two immiscible electrolyte solutions: Potential dependence of the ferro/ferricyanide-7,7,8,8-tetracyanoquinodimethane (TCNQ)/TCNQ⁻ system, *Phys. Chem. Chem. Phys.* 4 (2002) 3820–3827. doi:10.1039/b108882c.
- [30] F. Scholz, U. Schröder, R. Gulaboski, A. Doménech-Carbó, *Electrochemistry of Immobilized Particles and Droplets*, 2nd ed., Springer International Publishing, Cham, 2015. doi:10.1007/978-3-319-10843-8.
- [31] Vishwanath R.S, E. Witkowska Nery, M. Jönsson-Niedziółka, Electrochemistry of selected quinones at immiscible n-octyl-2-pyrrolidone/aqueous interface using a three-phase electrode system, *Electrochim. Acta.* 306 (2019) 54–60. doi:j.electacta.2019.03.095.
- [32] G. Inzelt, K. Németh, A. Róka, Electrochemical quartz crystal microbalance study of redox transformations of TCNQ microcrystals in concentrated LiCl solutions, *Electrochim. Acta.* 52 (2007) 4015–4023. doi:10.1016/j.electacta.2006.11.020.
- [33] M.F. Suárez, A.M. Bond, R.G. Compton, Significance of redistribution reactions detected by in situ atomic force microscopy during early stages of fast scan rate redox cycling experiments at a solid 7,7,8,8-tetracyanoquinodimethane-glassy carbon electrode-aqueous (electrolyte) interface, *J. Solid State Electrochem.* 4 (1999) 24–33. doi:10.1007/s100080050188.
- [34] A.M. Bond, K.B. Oldham, G.A. Snook, Use of the Ferrocene Oxidation Process To Provide Both Reference Electrode Potential Calibration and a Simple Measurement (via Semiintegration) of the Uncompensated Resistance in Cyclic Voltammetric Studies in High-Resistance Organic Solvents, *Anal. Chem.* 72 (2000) 3492–3496. doi:10.1021/ac000020j.
- [35] Z. Samec, E. Samcová, H.H. Girault, Ion amperometry at the interface between two immiscible

- electrolyte solutions in view of realizing the amperometric ion-selective electrode, *Talanta*. 63 (2004) 21–32. doi:10.1016/j.talanta.2003.11.023.
- [36] M.C. Grossel, A.J. Duke, D.B. Hibbert, I.K. Lewis, E.A. Seddon, P.N. Horton, S.C. Weston, An Investigation of the Factors that Influence the (TCNQ) and Its Salts to , and Structural Characterization of , the r , r -Dicyano- p -toluoylcyanide Anion, *Chem. Mater.* (2000) 2319–2323. doi:10.1021/cm991160g.
- [37] F. Quentel, V. Mirčeski, M. L’Her, Lutetium bis(tetra-tert-butylphthalocyaninato): A superior redox probe to study the transfer of anions and cations across the water|nitrobenzene interface by means of square-wave voltammetry at the three-phase electrode, *J. Phys. Chem. B*. 109 (2005) 1262–1267. doi:10.1021/jp045914c.
- [38] F. Scholz, R. Gulaboski, K. Caban, The determination of standard Gibbs energies of transfer of cations across the nitrobenzene|water interface using a three-phase electrode, *Electrochem. Commun.* 5 (2003) 929–934. doi:10.1016/j.elecom.2003.09.005.
- [39] P.M. Gross, The “Salting out” of Non-electrolytes from Aqueous Solutions., *Chem. Rev.* 13 (1933) 91–101. doi:10.1021/cr60044a007.
- [40] L.R. Melby, R.J. Harder, W.R. Hertler, W. Mahler, R.E. Benson, W.E. Mochel, Substituted Quinodimethans. II. Anion-Radical Derivatives and Complexes of 7, 7, 8, 8-Tetracyanoquinodimethan, *J. Am. Chem. Soc.* 84 (1962) 3374–3387. doi:10.1021/ja00876a029.
- [41] H. Kubota, Y. Takahashi, H. Hasegawa, T. Shimada, J. Harada, T. Inabe, Charge Carrier Doping into the Peierls Insulator of the TCNQ Anion Radical Salt (TCNQ = 7,7,8,8-Tetracyanoquinodimethane), *J. Phys. Chem. C*. 120 (2016) 11545–11551. doi:10.1021/acs.jpcc.6b02665.
- [42] M. Podrażka, J. Maciejewska, W. Adamiak, E. Witkowska Nery, M. Jönsson-Niedziółka, Facilitated cation transfer at a three-phase junction and its applicability for ionophore evaluation, *Electrochim. Acta*. 307 (2019) 326–333. doi:10.1016/j.electacta.2019.03.201.
- [43] F.M. Zanotto, R.A. Fernández, S.A. Dassie, Theoretical model of ion transfer-electron transfer coupled reactions at the thick-film modified electrodes, *J. Electroanal. Chem.* 784 (2017) 25–32. doi:10.1016/j.jelechem.2016.11.044.