1. Introduction

Capacitors are an important electronic device that can store and release electrical energy very quickly. Traditional capacitors consist of a dielectric layer sandwiched by two electrodes. By making the dielectric layer very thin, nano-capacitors have been explored both computationally and experimentally [1–4]. Due to their much larger capacity than traditional dielectric capacitors, supercapacitors store energy electrochemically and are playing important roles in electric energy storage [5, 6]. Two main types of supercapacitors are used: an electric double-layer capacitor (EDLC) stores energy in the electric double layer (EDL) and a pseudocapacitor stores energy via a surface redox process. Comparing with EDLCs, pseudocapacitor has higher energy density due to the advantage of redox reaction in charge storage [7–9].

Transition metal oxide is a typical electrode material to achieve pseudocapacitive energy storage due to its multivalent oxidation states [10–19]. In particular, ruthenium oxide has been studied for many years as a promising pseudocapacitor material [20–26].

Trasatti proposed that the charge storage mechanism of ruthenium oxide capacitor can be interpreted by the redox reaction: [21]

$$\text{RuO}_2(\text{OH})_x + z\text{H}^+ + ze^- \leftrightarrow \text{RuO}_{x-z}(\text{OH})_{x+z}.$$  

(1)

The oxidation state of Ru can be $+4$, $+3$ and $+2$ during the charge storage process, which could give a maximum theoretical capacitance over 1400 F g$^{-1}$ [9]. Experimental study on the RuO$_2$ pseudocapacitor showed that the measured capacitance from cyclic voltammetry (CV) is sensitive to the scan rate: a sharp redox peak showed up at low scan rate in the voltage of 0.1–0.4 V versus reverse hydrogen electrode, while at high scan rate the CV curve is rectangle [27, 28].
Specific capacitance of ruthenium oxide can also be greatly influenced by the particle size and the amount of structure water [28]. There have been many hypotheses for explaining the capacitive behavior of ruthenium oxide [29, 30], but first principles studies have been limited. Although classical simulations and theory have been successfully applied to model EDLCs [31–41], a first principles method such as electronic density functional theory (DFT) is needed to include the electronic structure and surface chemistry of the electrode into consideration when modeling RuO$_2$ pseudocapacitance. Although the DFT approach has been successfully applied to model the solid-state dielectric nanocapacitors [1–4], previous DFT calculations could not quantify the pseudocapacitance of RuO$_2$ from proton adsorption and intercalation [42, 43]. Directly calculating the Gibbs free energy of redox reaction could not accurately predict the electrode voltage of the reaction since it ignored the electrode-electrolyte interaction and the influence of overpotential [44].

To be able to accurately quantify the pseudocapacitance of RuO$_2$ from first principles, one needs to take into account both the EDL and redox mechanisms at the same time. To this end, herein we employ the joint density functional theory (JDFT) that allows us to examine the electrode/electrolyte interface self-consistently by treating the electrode at the electronic-structure level and the electrolyte classically. This approach enables us to calculate the electronic chemical potential shift with the surface redox reaction and to compute the differential capacitance versus the electrode voltage, thereby providing a capacitive curve from first principles that can be directly compared with the measured pseudocapacitive behavior. In section 2, we explain in detail the JDFT approach for the pseudocapacitive charge storage. Our main results are discussed in section 3, and we conclude in section 4.

2. Methods

Electronic chemical potential and total energy were calculated by JDFT in the JDFTx package with the implementation of linear polarizable continuum model (linear PCM) [45], which has been used in several theoretical electrochemical studies before [45–47]. Periodic boundary condition (supercell) was used to describe the solid/liquid interface: here we chose the most stable and active surface of rutile RuO$_2$, the (1 1 0) surface [48, 49], modeled in an orthogonal cell with $a = 6.24$ Å, $b = 12.74$ Å and $c = 25.14$ Å ($2 \times 2 \times 1$ supercell). The structural details about the RuO$_2$ crystal are provided in the supplementary data (see figure S1 and table S1 (stacks.iop.org/JPhysCM/28/464004/mmedia)). The space along the $c$ direction between two periodic slabs was filled with the implicit solvation model, as shown in figure 1(a). The generalized gradient approximation in the form of Perdew–Burke–Ernzerhof (GGA-PBE) functional was chosen to describe the exchange-correlation energy [50]. Ultrasoft pseudopotential was used to describe the nuclei-electron interaction [51]. The cutoff energy of plane wave basis set was 20 hartree in structure optimization and 30 hartree in electronic chemical potential calculation. The $k$-points mesh for Brillouin zone sampling was $4 \times 2 \times 1$ in structure optimization and $8 \times 4 \times 1$ in electronic chemical potential calculation.

In our simulation, the total capacitance is defined by the total charge over the electronic chemical potential shift: $Q_{\text{tot}}/\Delta \mu$ [52, 53]. The total charge ($Q_{\text{tot}}$) includes both Faradaic ($Q_{\text{F}}$) and non-Faradaic ($Q_{\text{EDL}}$) parts as shown in figure 1(b), corresponding to pseudocapacitance ($C_{\text{ps}}$) and EDL capacitance ($C_{\text{EDL}}$), respectively. Thus, it is important for us to determine how to assign $Q_{\text{F}}$ and $Q_{\text{EDL}}$ for a given $Q_{\text{tot}}$. To solve this problem, we propose a redox-EDL competition mechanism: at very low scan rate, the electrochemical behavior is at thermodynamic equilibrium and the capacitive behavior is dominated...
by thermodynamic energy preference. When the electrode is charged by a certain amount such as $1e^{-}$, we can compare the EDL energy ($U_{EDL}$) and hydrogen adsorption energy ($E_{H}$) to predict the capacitive behavior.

$U_{EDL}$ is defined by the energy drop of electrode to form the EDL to neutralize the surface charge of $1e^{-}$:

$$U_{EDL} = -\int_{V_1}^{V_2} C_{EDL} V dV,$$

(2)

where $V_1$ and $V_2$ correspond to the electronic chemical potential shift with the excess charge of $1e^{-}$. $E_{H}$, the hydrogen adsorption energy for a single H atom, is defined by:

$$E_{H} = U_{sub+H} - U_{sub} - \frac{1}{2} U_{H_2} + \Delta \text{ZPE},$$

(3)

where $U_{sub+H}$ and $U_{sub}$ are the total energy of H adsorbed substrate and bare substrate, respectively. $\Delta \text{ZPE}$ is the difference in zero point energy of hydrogen on the substrate and that of H$_2$ molecule. We use the $\Delta \text{ZPE}$ of 0.165 eV/H from previous DFT work [42]. For consecutive hydrogen adsorption, then we define $E_{H}(n)$, the hydrogen adsorption energy when $n$ H atoms have been absorbed on the substrate:

$$E_{H}(n) = U_{sub+(n+1)H} - U_{sub+nH} - \frac{1}{2} U_{H_2} + \Delta \text{ZPE}.$$

(4)

By comparing the $U_{EDL}$ and $E_{H}(n)$, we can estimate which way of charge storage is more preferable to neutralize the charged surface as we progressively charge up the electrode, as indicated in figure 2.

3. Results and discussion

First, we determine the potential of zero charge (PZC) and distinguish the different charge storage behavior of the anode and the cathode. Then, we focus on the capacitive behavior of the cathode. Since the EDL capacitance is always in existence as long as there is a charged surface, we will examine the intrinsic EDL capacitance of the RuO$_2$ (1 1 0) surface, and then compare the competition between EDL charge storage and redox charge storage on the cathode. Finally, based on the redox-EDL competition analysis, we will plot a capacitance-potential curve and provide a surface structure-based interpretation on the pseudocapacitive charge storage behavior of RuO$_2$(1 1 0).

3.1. Potential of zero charge on RuO$_2$(1 1 0)

We need to find out the potential of zero charge on RuO$_2$(1 1 0) in our system to assign potential region of positive and negative electrode charging behavior. For a pure RuO$_2$(1 1 0) surface in contact with a 1M implicit electrolyte, the calculated electronic chemical potential is $-4.70$ eV. This calculated electronic chemical potential comes from the total consequence of work function and implicit solvation model, while the zero potential is defined far inside the electrolyte. From the JDFT benchmark calculation, the standard hydrogen electrode (SHE) is at $-4.52$ eV with the GGA-PBE functional [45]. Thus, our calculated potential of zero charge (PZC) is $0.18$ V versus SHE. In addition, the calculated PZC is substrate thickness-independent. Experimental PZC of RuO$_2$(1 1 0) is $0.15$ V versus SHE in $10^{-3}$ M Na$_2$SO$_4$ [54], consistent with our DFT calculation. Here we should note that our PZC calculation is based on the electronic work function of the material with the consideration of solvation effect. The JDFTx code performs well when calculating the PZC by using linear PCM if there is no surface reaction that affects the PZC [45]. In the acidic electrolyte such as H$_2$SO$_4$, the PZC of transition metal oxide should be more positive so that it can resist proton adsorption to keep the surface neutral. When the electrode potential is higher than PZC, the electrode is positively charged and the capacitance is determined by the EDL because there is no available redox reaction of SO$_4^{2-}$ anion. Below the PZC, the electrode is negatively charged and the capacitance contribution is determined by the competition between the proton adsorption reaction and EDL. Thus, it is necessary to analyze the redox-EDL competition to determine the capacitive behavior of the cathode.
3.2. Influence of surface hydrogen adsorption on EDL capacitance

Since the EDL and redox reaction could simultaneously exist when the electrode is negatively charged, it is important to know how H adsorption influences the EDL capacitance. We calculated the EDL capacitance ($C_{\text{EDL}}$) of RuO$_2$(1 1 0) surface with different hydrogen coverage at various surface charge density range (figure 3). One can see that the EDL capacitance of a pure RuO$_2$(1 1 0) is about $19 \mu$F cm$^{-2}$, comparable to experimental measurement for aqueous electrolyte [55]. With the surface H adsorption, $C_{\text{EDL}}$ changed about $\pm 2 \mu$F cm$^{-2}$ within the first three H adsorption. The calculated electronic density of states (DOS) in figure 4 also showed that H-adsorbed RuO$_2$(1 1 0) is metallic and its DOS is very similar to that of clean RuO$_2$(1 1 0), while the site-projected DOS on the H atom (figure S2 in the supplementary data) shows that the H states are far deeper (more than 5 eV below the Fermi level). Thus, the electronic chemical potential shift is dominated by the electrolyte response (EDL capacitance). When the forth H is adsorbed on the surface, $C_{\text{EDL}}$ shows a large change and becomes very sensitive to charge. Since at the forth H adsorption, the electrode potential is close to that of hydrogen evolution on RuO$_2$, we mainly focus on the first three H adsorption.

3.3. Comparison of EDL energy and H adsorption energy

Based on the relatively constant $C_{\text{EDL}}$ for the first three H adsorption, we can calculate the EDL formation energy ($U_{\text{EDL}}$) by equation (2) and compare $U_{\text{EDL}}$ with the H adsorption energy ($E_H$) to predict the capacitive behavior. With the surface charge of $1e^-$, the charged electrode will be neutralized either by electric double layer (EDL) or H adsorption, so we plot the H adsorption energy with the EDL energy in figure 5. One can see that H adsorption should be more preferable than the EDL formation since the H adsorption energy is more negative than $U_{\text{EDL}}$. Consequently, we conclude that the pseudocapacitive behavior of RuO$_2$(1 1 0) is dominated by the surface redox reaction for the first few proton adsorption steps when the electrode is negatively charged:

$$\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_2 -x\text{(OH)}_x.$$ (5)

3.4. Capacitive behavior on RuO$_2$(1 1 0)

Now that we have found out the PZC and the preferred capacitive mechanism below PZC, the overall capacitive behavior should be: below PZC, redox reaction based on H adsorption; above PZC, EDL charge storage. The calculated charge–voltage ($Q$–$V$) and capacitance–voltage ($C$–$V$) curves are plotted in figure 6. The calculated PZC is 0.18 V versus SHE in the figure 6(a). In the redox reaction, each proton could provide the charge density of $10.07 \mu$C cm$^{-2}$. We calculated the electronic chemical potential shift after the redox reaction and the capacitance by $C = Q/\Delta\mu$. The pseudocapacitive region in the experimental $C$–$V$ curve is 0.1–0.4 V versus SHE, corresponding to the $-0.1$ to $0.2$ V
in our simulated C–V curve in figure 6(b), since we cannot take into account the influence of pH on the PZC calculation due to the limitation of implicit solvation model. The first two H adsorption could give the potential drop about 0.3V, which exactly matched the pseudocapacitive region in the experimental C–V curve [28]. Consequently, we propose that the experimentally measured pseudocapacitance of RuO2 at 0.1–0.4V versus SHE is contributed by the first two proton adsorption reaction in our simulation and the turning point in the C–V curve is due to the charge storage mechanism change from electric double layer to redox reaction at the PZC. The calculated areal capacitance is about 50–80 μF cm−2. It is expected that the capacitance will have a large increase when the electrode potential is more negative (still higher than the hydrogen evolution reaction potential), corresponding to the third H adsorption on the surface. The calculated capacitance for the third H adsorption (the slope of 2 H and 3 H in figure 6(a)) is over 260 μF cm−2. This very high capacitance is due to the surface phase transition and could be a reason to explain the extremely high capacitance in hydrous RuO2 nanoparticle, which will be discussed below. For the forth H adsorption on the surface, the calculated capacitance (the slope of 3 H and 4 H in figure 6(a)) decreases to 66 μF cm−2; here we note that the potential is negative enough (−0.4 versus SHE) that hydrogen evolution reaction may occur [57].

3.5. Adsorption structure of hydrogen on RuO2(1 1 0) and its influence on pseudocapacitance

Now we analyze the adsorption structures of H on RuO2(1 1 0) for the redox mechanism below PZC. For the first H adsorption step (figure 7(a)), the adsorption energy is about −1.0eV both on Oot (on top) and Obr (bridge) indicating that these two types of surface oxygen atoms show similar reactivity. The structure optimization after the second H adsorption also gave a perpendicular OH bond to surface (figure 7(b)) and H adsorption energy of −0.87eV. The perpendicular OH bond on RuO2(1 1 0) has been experimentally observed in basic condition [58]. The first and second hydrogen adsorption yielded a capacitance of 53.3 μF cm−2 (slope of 0 H and 1 H in figure 6(a)) and 81.9 μF cm−2 (slope of 1 H and 2 H in figure 6(a), respectively). When the third proton is adsorbed on the surface (figure 7(c)), it pushed the perpendicular OH bond on Oot to bended OH bond and caused the surface phase transition, but there was negligible change to the underlying RuO2(1 1 0) structure. Thus, the third H adsorption energy is below −2.0eV, which is much lower than the first two and closer to the previous DFT work [42]. The corresponding capacitance caused by the third H adsorption is 266 μF cm−2 (slope of 2 H and 3 H), an unexpectedly high value. When we put the forth H atom on the surface, the forth OH bond is perpendicular to the surface after structure optimization (figure 7(d)), and the corresponding capacitance is 66 μF cm−2 (slope of 3 H and 4 H). Consequently, we conclude that the capacitance provided by H adsorption reaction is structure-dependent: the perpendicular OH bond formation gives the capacitance about 60 μF cm−2 and the capacitance from bended OH bond formation is over 200 μF cm−2. This conclusion could be a possible interpretation of the experimentally observed size-dependent pseudocapacitance of RuO2 nanoparticle and high capacitance of hydrous RuO2 [27, 28]. When breaking down the crystal to small nanoparticles, it could have more Oα atoms that can form the bended OH bond, which can have higher capacitance than ideal surface. Hydrous RuO2 has had some H atoms and OH bond on the surface, so it could directly form bended OH bond instead of perpendicular OH bond at low H coverage.

Recently, Watanabe et al investigated the interfacial structure of RuO2(1 1 0) and water in different electrochemical conditions from first principles [59], and found that the orientation of OH bond and the surface coverage ratio of proton are strongly dependent on the pH and electrode potential. Our simulation was limited by the implicit solvation model where the ion is considered to be a point charge in the Debye screening theory and the solvent is a continuum dielectric medium with an electron density-dependent local
dielectric constant. In this electrode/electrolyte system, the JDFT method considers only the electrostatic interaction between the electrode and the electrolyte, so the ion/solvent interaction and hydration are not included, but the H\(^{+}\) ion is explicitly included via formation of the surface OH groups. In addition, the JDFT approach is intended to study the equilibrium properties, so the transport behavior such as diffusion cannot be examined. More advanced methods such as the effective-screening-medium method \[60\] can address the solvation and transport factors by including both the explicit solvation model and the ion dynamics. With such model, we expect that the bending angle of Ru–O–H would be influenced by the hydrogen bonding with water molecules in the electrolyte. Nevertheless, the present work provides a reasonable interpretation on the capacitive behavior of RuO\(_2\). When electrode potential is above PZC, measured capacitance is dominated by the electric double layer capacitance. Below the PZC, the capacitance is contributed by H adsorption reaction with low surface H coverage and perpendicular OH bond, which gives the capacitance of \(~60\ \mu\text{F cm}^{-2}\) as the electrode potential becomes more negative, surface phase transition happens due to the increasing H coverage and the bended OH bond formation produces a very high capacitance over 200 \(\mu\text{F cm}^{-2}\). These different capacitances of perpendicular and bended OH bond could explain why the small RuO\(_2\) nanoparticle

4. Summary and conclusions

Based on the JDFT with an implicit solvation model, we calculated the pseudocapacitive behavior of the RuO\(_2\) surface. Our calculated pseudocapacitance and corresponding voltage region show a qualitative agreement with the experimental CV curve, thereby providing a reasonable interpretation on the capacitive behavior of RuO\(_2\). The present work focused on the \((1\ 1\ 0)\) surface of RuO\(_2\). The experimentally synthesized RuO\(_2\) film has \((1\ 1\ 0)\), \((1\ 0\ 1)\), \((1\ 0\ 0)\), and \((1\ 0\ 1\ 0)\) facets: although these surfaces have close surface energies from DFT calculation, the surface energy of \((1\ 1\ 0)\) is the lowest \[48\]. That is why we chose this surface. It would be interesting to examine the pseudocapacitance on other surfaces as well. We expect that the specific values of capacitance would change for those different surfaces, but the general idea of coverage dependence and OH formation would still apply.
and hydrous RuO$_2$ have much higher capacitance than the RuO$_2$ film. Hence, our theoretical investigation provides an understanding of the pseudocapacitive charge storage behavior of the RuO$_2$ surface.

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