Role of Defects in Metal Oxides for Applications in Quantum Computing and Pseudocapacitive Charge Storage

by

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The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline.

Abstract

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Role of Defects in Metal Oxides for Applications in Quantum Computing and Pseudocapacitive Charge Storage

Thesis directed by Professor Charles B. Musgrave

The accurate prediction of materials properties and atomistic mechanisms is a significant challenge in condensed matter theory and computation that is made increasingly possible by *ab initio* methods. In this thesis we computationally investigate defects in metal oxides that are relevant to applications in quantum computing and pseudocapacitive charge storage.

We perform *ab initio* calculations of hydrogen-based tunneling defects in Al_2O_3 to identify deleterious two-level systems (TLS) in superconducting qubits. The formation energies of the defects are computed to give the likelihood of defect occurrence during growth. The potential energy surfaces and the corresponding dipole moments are evaluated to determine the coupling of the defects to an electric field. The tunneling energy is then computed for the hydrogen defect and the analogous deuterium defect, providing an estimate of the TLS energy and the corresponding frequency for photon absorption. We predict that hydrogenated

cation vacancy defects will form a significant density of GHz frequency TLS in Al_2O_3 .

Electrochemical supercapacitors utilizing pseudocapacitive materials offer the possibility of both high power density and high energy density. From first principles, we derive a detailed pseudocapacitive charge storage mechanism of MnO_2 and predict the effect of operating conditions on charge storage using a combined theoretical electrochemical and band structure analysis. We identify the importance of the band gap, work function, the point of zero charge, and the tunnel sizes of the electrode material, as well as the pH and stability window of the electrolyte in determining the charge storage viability of a given electrode material. The high capacity of α -MnO₂ results from cation induced charge-switching states in the band gap that overlap with the scanned potential allowed by the electrolyte. The charge-switching states originate from interstitial and substitutional cation defects. We calculate the equilibrium electrochemical potentials at which these states are reduced and predict the effect of the electrochemical operating conditions on their contribution to charge storage. The mechanism and theoretical approach we report is general and can identify new materials with high densities of thermodynamically accessible charge-switching states and optimal alignment of the relevant electrochemical potentials for improved pseudocapacitive charge storage.

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Chapter 1

Overview

1.1 A Materials Theory and Computation Perspective

Many technological advances have been driven by the discovery of new materials and their properties. Unfortunately, materials discovery and optimization by Edisonian or combinatorial methods can be both time and resource consuming. In materials theory and computation, and for atomistic *ab initio* computational methods in particular, materials properties and phenomena are routinely elucidated from the inputs of initial conditions and employing quantum chemical approximations, such as density functional theory [1, 2], to solve the equations of quantum mechanics[3]. These methods have facilitated the prediction of fundamental properties, mechanisms and other related phenomena to enable the virtual experimentation on materials *in silico* [4, 5], accelerating both our understanding and rate of discovery for materials encompassing multiple fields and technologies. This approach has already proven effective in identifying and understanding materials for applications in energy storage [6, 7], catalysis [8], photovoltaics [9], photoelectrochemical water splitting [10, 11], hydrogen storage [12, 13], CO_2 capture [14], topological insulators [15], and thermoelectrics [16].

First principles computations continue to be an integral part of characterizing materials and defect properties, and in a number of areas theory has led experiment in understanding and guiding the development of these aspects of materials. In this thesis, we will demonstrate the accurate prediction of materials properties and atomistic mechanisms using *ab initio* methods for two important applications in emerging technologies. Our goal is to provide the fundamental understanding of these properties and mechanisms to enable the discovery of improved materials for the next generation of energy storage systems and advanced quantum electronics.

1.2 Overview of Thesis

In this thesis, I discuss the application of computational materials theory to investigate dielectric loss in qubit materials and pseudocapacitance in charge storage materials. Chapter 2 provides an introduction and background to the computational methods and defect theory used throughout the thesis. Chapter 3 is divided into two parts. In the first part of chapter 3 I introduce superconducting qubit materials and the two-level system model for dissipative loss in these materials. I then discuss the evidence for hydrogen as a candidate defect for dielectric loss in alumina and describe a simplified model to explain rotational defects and their energy spectrum. In the second part of chapter 3 I discuss our investigation of bulk and surface tunneling hydrogen defects in alumina. This begins with a brief discussion of the computational details relevant for predicting the defect properties in this system and then reports the computed defect formation and tunneling properties. I conclude chapter 3 with a discussion of the identified defect contribution to dissipative loss and their broader implications. Chapter 4 discusses the mechanism of pseudocapacitance in manganese oxide, and is divided into three parts. In the first part I introduce pseudocapacitance and our proposed model for understanding it. I then review the background and pertinent experimental observations reported for manganese dioxide pseudocapacitors. In the second part of chapter 4 I discuss the integrated electrochemical and band structure theory and computations we have implemented to investigate the mechanism of pseudocapacitance. In the third part of chapter 4 I report the detailed mechanism we have developed for pseudocapacitance in manganese dioxide and its broader impacts for studying and identifying other electrochemical charge storage materials. Finally, in chapter 5, I conclude with a summary of our findings and offer some forward looking remarks.

Chapter 2

Defect Formation Energies and Computational Methods

2.1 Defect Formation Energies

The accurate prediction of materials properties and atomistic mechanisms is a significant challenge in condensed matter theory and computation that is made increasingly possible by *ab initio* methods. In particular, reliable calculation of defect properties remains a significant challenge that is limited by the state of the art in both the approximations of the theory and the computational hardware that makes these calculations tractable. In this thesis, we focus on the use of screened hybrid density functional theory (DFT) in predicting the properties of defects in metal oxides and understanding their role in quantum computing and pseudocapactive charge storage applications.

To predict defect properties the important quantity to calculate accurately is their formation energies (E_f) , which is derived from total energy calculations [17, 18] using the same basis set or planewave cutoff, *k*-point grid, etc. to take advantage of the cancellation of errors. The equilibrium concentration of noninteracting defects is related to their formation energies by the Boltzmann expression $c = me^{-E_f/kT}$, where m is the multiplicity of equivalent sites per unit volume in the system where the defect may occur. For a given defect D in charge state q the defect formation energy, $E_f(\mu_i, \mu_e) = E_T^{D,q} - E_T^{H,q} - \sum_i \Delta n_i \mu_i + q\mu_e$, is a function of the chemical potentials of the constituent elements μ_i and electrons $\mu_e, E_T^{D,q}$ and $E_T^{H,q}$ are the calculated total energies of the defect and host supercells, respectively, and Δn_i is the change in the number of atoms of element i in forming the defect.

The range of chemical potentials of the elements μ_i viable for metal oxide formation are constrained by equilibrium conditions relating the chemical reservoirs used to represent experimental conditions of the constituent atoms during formation. For a metal oxide, the values of μ_i are bounded by the metal-rich and O-rich conditions, and the stability relation imposed by the formation enthalpy $\Delta H_f(M_{N_M}O_{N_O}) = N_M\mu_M + N_O\mu_O$. $\Delta H_f(M_{N_M}O_{N_O})$ is determined from total energy calculations of the metal-oxide in crystalline form and the constituent atoms in their reference states. The introduction of impurities, such as hydrogen or other cations is accounted for by including the formation of water or other alkali metal hydroxide as a limiting phase [19] by their aqueous stability relations. Defect formation energies vary considerably with the Fermi level of the system. This is because the chemical potential for electrons is the Fermi level, which by convention in defect formation energy plotting is set to zero at the valence band maximum (VBM). A major limitation of local (local density approximation) and semi-local (generalized gradient approximation) DFT is that these methods significantly underestimate bandgaps. A failure to correctly describe the energetic position of the band gap hinders the accuracy of predicted defect properties because the defect levels are sensitive to the position of the band edges. In section 2.2 we discuss how screened hybrid DFT is able to overcome this limitation and provide accurate prediction of defect properties.

Defect calculations using *ab initio* methods and supercell approaches must give consideration of to the effects due to the finite supercell size and compensating background charge used to describe charged defects. Unfortunately, in order to simulate a defect density of 10^{18} /cm³ it would require an atomistic model of 1 defect per ~20,000 atoms, which is still beyond the computational feasibility for tractable DFT calculations. Therefore, the effective defect concentrations used in supercell approaches tend to be higher than those observed experimentally. This requires the effects due to the finite supercell size and charged defect compensation to be accounted for and corrected. A reliable approach to apply these finite size corrections is to relate the defect supercells relative to the host supercell by using the differences in average electrostatic potential to align the band edges [20, 21]. Once this correction has been performed, the defect formation energies and charge switching levels of the defects can be accurately determined. An illustrative example is shown in Figure 2.1 of the plotting and reporting of defect properties that will be used throughout this thesis.



Figure 2.1 from Ref. [18] : Plot of the defect formation energies under Ga-rich conditions for the lowest energy charge state as a function of Fermi level for interstitial (X_i), vacancy (V_x), and antisite (N_x) defects, where X=Ga or N, in GaN. The zero of the Fermi level corresponds to the valence band maximum.

In this plot, the defect formation energies for interstitial (X_i) , vacancy (V_x) , and antisite (N_x) defects, where X=Ga or N, are plotted for GaN under Ga-rich conditions. Only the lowest energy form of the charged defects is depicted, and each change in slope represents a transition in the defect charge state. The charge switching levels corresponding to the different charge states for each defect type shown in Figure 2.1 are illustrated in Figure 2.2. We will report the charge switching and formation energies for defects in Al₂O₃ and MnO₂ in chapters 3 and 4, respectively.



Figure 2.2 from Ref. [18]: Thermodynamic charge switching levels relative to the band edges of GaN and determined from defect formation energies of the native defects shown in Figure 2.1.

2.2 Computational Methods

The ability to reliably predict and explain the properties of materials has significantly advanced decade by decade with the implementation of new developments in electronic structure theory and methods. Some of the early and most influential results for materials predictions from electronic structure calculations were performed using the local and semi-local approximations to DFT. Even though these approximations to DFT are proven methods and still provide useful predictions for many properties and systems, they are unreliable for predicting electronic band gaps. For example, the inadequate description of strong Coulomb correlations due to localized electrons in systems such as metal oxides has led to the underestimation of the band gap in these materials, even to the extent of predicting metallic solutions for systems that are known experimentally to be insulators [22], [23].

The principle of DFT is based on the Hohenberg-Kohn theorem [2] that specifies the ground state charge density of a system of interacting fermions and ion potentials uniquely determines the Hamiltonian and therefore ground state energy of the system. The Kohn-Sham formulism of DFT [1] recasts the intractable problem of solving the Schrödinger equation of interacting particles into a single particle effective theory that is tractable. Although the kinetic, Coulomb, exchange, and correlation energies are a universal functional of the charge density, the exact definition for each potential is not known, and thus different approximations are invoked to describe these potentials with differing degrees of accuracy and computational feasibility. As previously mentioned, the local and semi-local approximations of DFT tend to underestimate the band gap of materials, or stated otherwise, that the difference in the corresponding eigenvalues of solving the Kohn-Sham equation for materials are significantly below the experimentally determined values for the valence and conduction bands. In contrast, Hartree-Fock (HF) theory, which is also an effective single particle theory, treats exchange in an exact nonlocal manner, which tends to result in HF overestimating electronic band gaps. Therefore, it is plausible that a theoretical description that combines both DFT and HF, known as hybrid DFT, can provide a more accurate description of materials electronic structure and properties.

Indeed, it has been demonstrated that mixing in exact exchange with the DFT method compensates for the self-interaction error introduced by semilocal exchange functionals in describing band gaps and defects [24, 25]. Additionally, the nonlocal portion of the HF exchange can be truncated by screening the range over which it is computed to reduce computational cost and still provide quantitative accuracy. This is the motivation behind the Heyd-Scuseria-Ernzerhof hybrid exchange-correlation functional (HSE), which has demonstrated improved accuracy for predicting semiconductor and insulator properties [26-28]. Therefore, in this thesis we employ HSE for all defect calculations with the amount of exact exchange in the HSE functional adjusted to reproduce experimental band gaps when known,

or the reliable results of partially self-consistent GW_0 quasiparticle calculations [29, 30] when experimentally unknown; the specific details to each study are reported in their respective chapters

Chapter 3

Tunneling Hydrogen Defects in Alumina

3.1 Introduction

3.1.1 Two-Level Systems in Qubit Materials

Superconducting qubits and resonators allow simple quantum information algorithms to be performed in integrated circuits [31, 32]. Unfortunately, the performance of these circuits is limited by decoherence caused by resonant two-level system (TLS) defects. These appear in dielectrics, such as in the alumina barrier of a Josephson junction [33, 34], interlayer dielectrics [34, 35], and in native oxides found on various substrate and superconductor surfaces [36, 37]. As a result, the development of quantum integrated circuit technology depends on reducing these parasitic defects. In addition, because many types of defects are expected in integrated circuits, it is essential to identify the two-level systems to avoid exhaustive heuristic searches for new processes and materials. Shown in Figure 3.1 is a state of the art nine element quantum processor fabricated on a sapphire substrate using Al/Al₂O₃/Al Josephson junctions from Ref. [32]. Of particular note is the importance of aluminum oxide in the fabrication of these devices, which still suffer severely from decoherence processes [32].



Figure 3.1 from Ref [2]: micrograph of a nine element quantum processor (coloured) fabricated on a sapphire substrate (dark) using $Al/Al_2O_3/Al$ Josephson phase qubits (Q₁₋₄) and operated at 25 mK.

In amorphous materials, including dielectrics, the conventional TLS model describes observed low-temperature behavior in terms of a distribution of tunneling defects [38-40]. Despite later refinements to the theory [41-43], the specific atoms or groups of atoms which tunnel are generally unknown. Arguably the best characterized amorphous dielectric is SiO₂, where TLS phenomena are well established by specific heat [44] and dielectric measurements [45]. In electric spin echo measurements, a TLS dipole moment from the GHz regime was found to be correlated with OH-concentration [46]. Room temperature far infrared absorption spectra, measured above the frequency of the known free OH rotor absorption, interpreted the OH motion as partial rotations around a central SiO bond due to configurations and tunneling in the solid environment [47]. By using a double well potential model Phillips et al. (illustrated in Figure 3.2) concluded that the same potential would produce a 3.7 GHz frequency difference in the lowest two energy states [48], establishing a widely accepted physical model of a TLS in the GHz regime.



Figure 3.2: Illustration of a symmetric (top left) and asymmetric (top right) double well potential model with a tunnel barrier (V₀) for two-level systems (TLS). Both the tunneling (Δ_0) and asymmetry (Δ) energies contribute to the energy differences between the two lowest states of the system. A model Hamiltonian (bottom right) was derived by Hunklinger *et. al.* [45] to describe a TLS with a dipole moment (*p*) in a dielectric media interacting with the an electric field of a capacitor (bottom left).

3.1.2 Evidence for Hydrogen TLS in Alumina

Of particular interest to superconducting qubits is alumina, including amorphous Al₂O₃. In the majority of superconducting qubits this material is used as the Josephson junction tunnel barrier, as the substrate material, and also appears as the native oxide of the aluminum wiring [33, 34, 37, 43]. In the alumina Josephson junction barrier, TLS are found to be consistent with the tunneling motion of OH, which are comparable to the OH-related TLS in SiO_2 [35, 49]. In addition, dielectric relaxation measurements of Al₂O₃ films show that TLS density increases monotonically with H_2 exposure [50]. Evidence for hydrogen TLS in atomic layer deposition grown metal oxide films has been deduced from secondary ion mass spectrometry (SIMS) composition studies and low temperature millikelvin microwave loss measurements [51]. The SIMS impurity concentration profiles are shown in Figure 3.3 (top) and the corresponding internal quality factor (1/Q)determined for each film type are shown in Figure 3.3 (bottom) from Ref. [51]. Although hydrogen is clearly indicated as a TLS defect in qubits, acting as an OH rotor or a more complicated structure, a full physical model of a TLS is still lacking.





Figure 3.3: (top) Hydrogen impurity concentration measured by SIMS from Ref.[51] for films with nominally identical parameters to those shown in the figure below, as well as C impurity concentration in c-BeO film. The crystalline BeO film (75 nm thick) shows a large H concentration that is nearly uniform throughout the film depth, while the $a-Al_2O_3$ and $a-LaAlO_3$ films (each approximately 48 nm thick) show H concentrated at the surface of the films. The c-BeO film also shows a large surface distribution of C impurities. (bottom) Inverse internal quality factor (1/Q) of coplanar strip resonators on three film types from Ref.[51].

3.1.3 Model System for a Tunneling Rotor Defect

Before discussing tunneling defects in bulk and surface α -Al₂O₃ we first employ a minimal OH rotor model constructed from an Al(OH)₃ molecule to illustrate the microscopic tunneling behavior of hydrogen in this system. Rotation of an OH group in Al(OH)₃ about the Al-O bond, with the other two OH groups symmetrically oriented, results in a periodic double-well potential for the rotational motion. As shown in Figure 3.4, we find that this leads to a rotational barrier of 121 meV, and that hybrid density functional theory (PBE0) reproduces the more accurate coupled cluster (CCSD(T)) method for this system, and is thus well suited for describing this interaction.



Figure 3.4: Rotational potential energy surface (PES) for an OH group in $Al(OH)_3$ employed as a pedagogical model for a tunneling defect in Al_2O_3 . We find that hybrid DFT is well suited for describing this system by reproducing the results of the more accurate coupled cluster method.

Solving the Mathieu equation (discussed in section 3.2.3) results in a tunneling energy (Δ_0 in the TLS model described in section 3.1.1) of 3.6 x 10-3 meV, or ~ 1 GHz, for the OH rotor in Al(OH)₃; which is on the order of the ~6 GHz loss observed experimentally [51], and suggests H based rotor in Al₂O₃ are a candidate defect for contributing to TLS loss. Additionally, it is found that an equivalent deuterium rotor (OD) has a much lower tunneling energy and probability (Figure 3.5), suggesting deuterium substitution may provide a route for eliminating loss in the microwave regime due to hydrogen defects in Al₂O₃.



Figure 3.5: Energies of the ground and first excited states of the OH and OD rotors of the simplistic $Al(OH)_3$ model system. We find that the tunneling energy (bottom) and probability (top) for the OD rotor is significantly reduced as compared to the OH, and thus OD rotors are not expected to contribute loss in the GHz regime.

This simplistic $Al(OH)_3$ model suggests that hydrogen based defects in Al_2O_3 acting as tunneling rotors may be a source of TLS loss. Next, we employ two interacting Al(OH)₃ rotor models to investigate how the electrostatic interaction between the rotors changes their corresponding rotational potential energy surface. We find that at rotor distances beyond 7 Å the perturbation to the rotational potential energy surface is sufficiently small and beyond the resolution of our methods (shown in the 1D rotor PES of figure 3.6 (top) and 2D rotor PES of Figure 3.6(bottom)). This distance informs the system size we employ in our more sophisticated bulk and surface Al₂O₃ models to aid in minimizing undesired defectdefect interactions, which are further screened in the bulk by the higher dielectric of Al_2O_3 as compared to the vacuum dielectric in the simplistic model. Additionally, we find that the rotor becomes localized in a single well minimum as the distance between rotors is decreased, suggesting that at high defect densities some rotor defects may also become localized, which could eliminate their tunneling TLS character and contribution to TLS loss.




Figure 3.6: (top) 1D PES for interacting OH rotors of two Al(OH)3 model systems. (bottom) Corresponding 2D PES at isolated and 4 Å distances.

3.2 Bulk and Surface Tunneling H Defects in Al₂O₃

3.2.1 Computational Details

To provide a more complete description of TLS loss in qubit materials, we have calculated and identified bulk and surface hydrogen defects of alumina using *ab initio* techniques. Here, we discuss bulk hydrogenated Al vacancies and interstitial hydrogen coordinated to six adjacent O atoms in the α -Al₂O₃ crystal. We also consider a surface OH rotor, where the O is attached to a surface Al atom on an alumina crystal to form a solid surface analog of the canonical OH rotor. We calculate the formation energies, tunneling energies and dipole moments of the defects. Furthermore we predict the significance of these defects as TLS to devices in the GHz and THz regimes.

Electronic structure calculations were performed using hybrid density functional theory with the screened hybrid HSE06 functional [26, 27] and the projector augmented-wave (PAW) method [52] as implemented in the Vienna Ab initio Simulation Program (VASP) [53-55]. PAWs were used to describe the valence electrons explicitly while pseudopotentials were used to model the core electrons. To reproduce the experimental band gap of α -Al₂O₃, the amount of exact exchange was adjusted to 32% in HSE06 using the standard range separation parameter. The exchange adjustment did not significantly impact the predicted lattice parameters, and the calculated properties are in close agreement with experiment, as summarized in Table 3.1.

Table 3.1: Calculated lattice parameters, direct band gap and formation enthalpy of α -Al₂O₃ with experimental values listed for comparison. Calculations were performed using a 30 atom supercell with a 2×2×1 grid of Γ -centered k-points and a 500 eV plane wave cutoff energy.

α -Al ₂ O ₃	HSE06(32%HF)	Expt
a (Å)	4.73	4.76^{a}
c (Å)	12.96	12.98^{a}
Bandgap (eV)	8.88	8.80^{b}
ΔH_{f} (eV/f.u.)	-16.39	-17.36^{c}

a ref. [56], *b* ref. [57], *c* ref. [58]

All bulk Al and Al₂O₃, and molecular O₂, H₂, and H₂O calculations were spin polarized and performed with a 500 eV plane wave cutoff energy and computed to sub-meV convergence. The bulk properties of α -Al₂O₃ were calculated using a 30 atom supercell with a 2×2×1 grid of Γ -centered k-points. Supercells for defect calculations were constructed by extending the 30-atom cell; A 2×2 120-atom supercell (Figure 3.7a) was employed for bulk defect calculations. For surface defects, an 84-atom surface supercell (Figure 3.7b) was constructed by cutting the 120-atom supercell along the (0001) plane to create a charge neutral single layer Al termination of the surface in agreement with the experimentally identified stable surface termination of vacuum grown Al₂O₃ [59, 60]. A vacuum gap of 12 Å was used in the surface supercell and the atoms in the bottom four layers (two O layers, and two Al layers) were constrained to their bulk positions during all calculations. All defect calculations were conducted at the Γ -point.



Figure 3.7: Structure of Al_2O_3 supercells used in the bulk and surface tunneling hydrogen defect study. (a) View along the c axis (top) and perpendicular side view (bottom) of the 120-atom bulk supercell and (b) view along the b axis of the 84-atom surface supercell. Al atoms are shown in gray and O atoms are shown in red.

We first identified defects of sufficient concentration to contribute to TLS loss by calculating their formation energies (E_f) derived from total energy calculations [17]. The equilibrium concentration of non-interacting defects is related to their formation energies by the Boltzmann expression $c = me^{-E_f/kT}$, where m is the multiplicity of equivalent sites per unit volume in the system where the defect may occur. For a given defect D in charge state q the defect formation energy, $E_f(\mu_i, \mu_e) =$ $E_T^{D,q} - E_T^{H,q} - \sum_i \Delta n_i \mu_i + q\mu_e$, is a function of the chemical potentials of the constituent elements μ_i and electrons $\mu_e, E_T^{D,q}$ and $E_T^{H,q}$ are the calculated total energies of the defect and host supercells, respectively, and Δn_i is the change in the number of atoms of element i in forming the defect.

The range of chemical potentials of the elements μ_i viable for metal oxide formation are constrained by equilibrium conditions relating the chemical reservoirs used to represent experimental conditions of the constituent atoms during formation. For a metal oxide, the values of μ_i are bounded by the metal-rich and O-rich conditions, and the stability relation imposed by the formation enthalpy $\Delta H_f(M_{N_M}O_{N_O}) = N_M\mu_M + N_O\mu_O$. We determine $\Delta H_f(M_{N_M}O_{N_O})$ from total energy calculations of the metal-oxide in crystalline form and the constituent atoms in their reference states. We found $\Delta H_f(Al_2O_3)$ to be -16.39 eV/formula unit, in good agreement with the experimental value of -17.36 eV/f.u. [58]. The introduction of impurities such as hydrogen is accounted for by including the formation of water as a limiting phase [19] by the stability relation $2\mu_H + \mu_0 \leq$ $\Delta H_f(H_2O)$. We determine $\Delta H_f(H_2O)$ by a gas-phase calculation, leading to a formation enthalpy of -2.68 eV/molecule, and agrees well with the experimentally determined value of -2.51 eV/molecule [58]. We accounted for effects due to the finite supercell size and compensating background charge of charged defect supercells relative to the host supercell by using the differences in average electrostatic potential to align the band edges [20, 21].

3.2.2 Hydrogen Defect Formation Energies

We plot the predicted defect formation energies for the lowest energy charge state as a function of Fermi level and under both O-rich and Al-rich growth conditions in Figure 3.8 for bulk and surface defects of α -Al₂O₃.



Figure 3.8: Defect formation energies (E_f) under O-Rich (left) and Al-Rich (right) growth conditions for interstitial H (purple), surface OH (orange), Al vacancy (dashed-red), and hydrogenated Al vacancy (blue) defects in α -Al₂O₃ as a function of Fermi level. Only the lowest energy charge state is shown for each defect type within the band gap for α -Al₂O₃. Interstitial H₂ (green) provided as a reference. Calculations were conducted at the Γ -point using 120 and 84 atom bulk and surface supercells with 500 eV plane wave cutoff energies.

Surface hydroxylation $[OH_{surf}]$ is found to be favorable under all growth conditions, suggesting that hydroxide termination at interfaces and of surfaces of Al₂O₃ will occur when exposed to water [61]. The resulting surface OH rotor is found to have three degenerate local minima along the rotor path. The formation of a bulk Al vacancy $[V_{Al}]^q$ results in the formation of six nearest neighbor oxygen dangling bonds near the valence band maximum. For neutral Al vacancies (q = 0) the O dangling bonds are occupied by three holes which become populated with increasing Fermi level (E_F), creating the charge states q = -1, -2, and -3, the most energetically favorable $[V_{Al}]^q$ defect. Hydrogenation of the bulk Al vacancy by H⁺ $[V_{Al}-H^+]^q$ creates a stable defect with charge ranging from q = +1 at the valence band maximum to q = -2, the most favorable charge across the widest range of E_F . The charge state of nearest neighbor O atoms becomes more negative with increasing E_F , leading to tighter binding with the H⁺ defect. This results in differing structural relaxations with changing charge state, and indicates that the hydrogenated defect will have properties dependent on the charge state. Although crystalline Al₂O₃ is considered to be a low loss dielectric material [62], under O-rich conditions the formation of hydrogenated Al vacancy defects is found to be energetically favorable and our results suggest that these defect types should be common in amorphous Al₂O₃.

We predict interstitial hydrogen defects $[H_{int}]^q$ to occur in significant concentration in Al₂O₃ at low E_F for both O-rich and Al-rich growth conditions. The stable form of interstitial hydrogen under these conditions is H⁺, where the H⁺ is localized to one of its six nearest neighbor oxygen atoms. As E_F increases the H⁺ defect changes charge state to an H⁻; the neutral charge state H is never the most stable form of this defect. Upon formation of H⁻, structural relaxation causes H⁻ to no longer bond to a nearest neighbor oxygen but to instead occupy a defect site equidistant from its six nearest neighbor O atoms. In contrast, interstitial H⁺ has six degenerate local minima, each localized at one of its six nearest neighbor O atoms. The adjacent minima for interstitial H⁻ are much further apart than the minima of H⁺, indicating that interstitial H⁺ defects are significantly more likely to tunnel than interstitial H⁻ defects in Al_2O_3 . Interstitial molecular H₂ was not found to be energetically viable under any growth conditions.

3.2.3 Defect Tunneling Properties

The conventional TLS model in amorphous solids is based on atoms tunneling between two neighboring potential wells [38-40]. Although higher symmetry multi-well potentials exist in the crystalline form, local strain in amorphous materials is expected to distort these potentials to the double-well form. In this model, the number density distribution $d^2n = P_0 d\Delta d\Delta_0/\Delta_0$ depends on the defect's tunneling energy Δ_0 , asymmetry energy Δ and material constant P_0 . In this model the TLS energy $E_{TLS} = \sqrt{\Delta_0^2 + \Delta^2}$ is larger than the tunneling energy due to contribution from the asymmetry energy. However, the resonant field loss from a TLS is proportional to Δ_0^2/E_{TLS}^2 , such that the TLS coupling to fields is largest when asymmetry is the smallest [47]. Therefore, we expect that the center of the measured broad TLS energy distribution produced by an amorphous solid defect will be approximately equal to the tunneling energy Δ_0 calculated for the same defect in the corresponding crystal. We determine defect tunneling from the structurally relaxed minimum energy pathway (MEP) between defect potential minima using the nudged elastic band procedure [63] for each charge state of the viable hydrogen based defects. The inherent C₃ symmetry axis perpendicular to the (0001) face and local S₆ symmetry points in α -Al₂O₃ suggest that defects formed in this material may exhibit 3-fold or 6-fold symmetric rotational character about this axis corresponding to the migration between degenerate localized defect sites. We found that surface hydroxides (OH), hydrogenated Al vacancies and interstitial H all followed a MEP corresponding to a quantum rotor (Figure 3.9). We next determined the defect tunneling energy by fitting the calculated MEP to a rotational Hamiltonian, $H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\theta^2} + V_0 \cos(j\theta)$, involving *j* rotational minima (Figure 3.10),



Figure 3.9: (a) Tunneling bulk and surface H (blue) rotor defects identified in α -Al₂O₃ viewed partially off axis in the [0001] direction. Dashed circles indicate rotor MEP. Blue encircled O atoms (red) indicate the local rotor minima. (b) View along the rotational axis of the H tunneling defects and the O nearest neighbors that create the rotor local minima. (c) View perpendicular to the H defect rotational axis and O nearest neighbors illustrating rotational plane parallel to the (0001) plane in α -Al₂O₃. (left) OH rotor bound to a surface Al (gray) resulting in a 3-fold degenerate rotor. (center) Hydrogenated Al bulk vacancy defect resulting in the formation of a 3-fold degenerate H⁺ rotor. (right) Interstitial H⁺ with six O nearest neighbors that form a 6-fold degenerate rotor.



Figure 3.10: 3-fold degenerate relaxed PES of hydrogenated charged Al vacancies in Al_2O_3 . PES calculated along the MEP for transitions of H between minima and fit to an analytic function to solve for the TLS properties (Table 3.2).

For j = 2, this equation is an exactly solvable Mathieu equation with eigenfunctions of the form of symmetric and antisymmetric combinations of the single-well ground state wavefunctions (localized basis), and are denoted as E_{0k} , where k = 0 or 1 to indicate the symmetric ground state or antisymmetric first excited state solutions. The transmission of the eigenfunctions through the barrier induces an energy splitting Δ_0 between the 0 and 1 levels of the quantum rotor TLS.

We extended the application of the Mathieu equation to model 3-fold and 6fold symmetric rotors by a linear transform, $j\theta \rightarrow 2\theta'$. This approach only identifies the fully symmetric and fully antisymmetric eigenfunctions for both the 3-fold and 6-fold degenerate rotor potentials. A 3-fold degenerate rotor potential has three solutions in the localized basis, the k = 0 ground state and the $k = \pm 1$ doubly degenerate first excited state solutions, where only the k = -1 state is not determined from solution of the Mathieu equation. Thus, this approach provides a valid approximation for determining Δ_0 of a 3-fold degenerate rotor [64].

An additional approximation is applied to solve for Δ_0 of a 6-fold degenerate rotor potential, in which two pairs of degenerate levels exist among the set of six solutions in the localized basis, $k = 0, \pm 1, \pm 2$, and 3. Here, mapping the 6-fold potential to the form of a Mathieu equation identifies the 0 and 3 eigenfunctions. Therefore, our reported Δ_0 for these defects is approximated by treating the ± 1 and ± 2 solutions as being evenly spaced between E_{00} and E_{03} so that $\Delta_0 = (E_{03} - E_{00})/3$. Furthermore, the higher order degeneracy of the rotors may be reduced to that of a double well potential by additional environmental disorder due to strain or interactions with other defects. However, even for large shifts in the asymmetry energy Δ only a small perturbation to the potential barrier V₀ occurs, suggesting that the double-well tunneling energies would be lower by a factor on the order of unity from our calculated values.

Table 3.2: Calculated properties for each tunneling H defect type and charge state in Al₂O₃ identified in this study. The rotor radius (R) and potential barriers (V₀) are computed from the structurally relaxed rotor MEP. Dipole moments (p) are derived from the displacement between rotor potential well minima and a corresponding charge analysis. Calculated tunneling splitting energies (Δ_0) for identical hydrogen (H) and deuterium (D) substituted defects are reported in GHz.

Defect	R(pm)	p(D)	V ₀ (meV)	$\frac{\Delta_{0,H}}{h}$ (GHz)	$\frac{\Delta_{0,D}}{h}$ (GHz)
OH_{surf}	76	3.2	19.1	$1.0 \ge 10^3$	$2.8 \ge 10^2$
$[V_{Al}-H^+]^{+1}$	71	3.0	214	$1.3 \ge 10^{1}$	$2.1 \ge 10^{-1}$
$[V_{Al}-H^+]^0$	71	3.0	480	$2.1 \ge 10^{-1}$	4.9 x 10 ⁻⁴
$[V_{Al}-H^+]^{-1}$	68	2.8	731	$2.2 \ge 10^{-2}$	$1.7 \ge 10^{-5}$
$[V_{Al}-H^+]^{-2}$	67	2.8	612	$1.0 \ge 10^{-1}$	$1.5 \ge 10^{-4}$
$[H_{int}]^{+1}$	95	2.3	152	$^{a}2.4 \ge 10^{2}$	$^{a}2.3x\ 10^{1}$
$[H_{int}]^0$	-	-	$^{b}1300$	-	-
[H _{int}]-1	-	-	^b 1420	-	-

a Forms a 6-fold degenerate rotor defect (*vide infra*)

b Does not form a rotor defect (see Figure 3.11)

Table 3.2 shows our calculated H-based defect rotor properties. Bader charge analysis [65, 66] was performed to identify the charge on the tunneling atoms along the MEP. The dipole moment p was determined using the tunneling distance between local minima and the H atom charge. The surface dipole moment was found to be the largest at 3.2 Debye. The moment of the bulk defects is only slightly smaller such that they could all couple strongly to Josephson junction qubits. For the hydrogenated cation defect the moment depends on charge such that the low and high charge states should be distinguishable. As previously above, the adjacent minima for interstitial H and H^{\cdot} are much further apart than the minima of H⁺. This results in a translational MEP between the neighboring defect sites corresponding to the interstitial H and H^{\cdot} minima, as depicted in Figure 3.11.



Figure 3.11: Translational minimum energy pathway identified between defect sites for interstitial H and H^{\cdot}. No corresponding rotor defect was identified for these species and they are not expected to contribute to loss in the GHz regime. Points along the pathway are depicted by the H/H^{\cdot} (shown in blue) moving between neighboring sets of oxygen atoms (shown in red, Al is shown in gray).

3.2.4 Defect Contribution to TLS Loss

OH surface defects are found to form a 3-fold degenerate tunneling rotor with a tunneling barrier of only 19.1 meV between local minima. This leads to an energy

splitting in the THz regime due to tunneling between the ground and first excited states of the rotor. However, the favorable defect formation energy for hydroxylation of the Al_2O_3 surface and lack of dielectric screening between the rotor and its environment suggest that the potential energy surface of the rotor is readily perturbed by defect interactions [67]. Thus, it is expected that surface OH rotors will create GHz loss in superconducting devices.

Hydrogenated Al vacancies are predicted to exist in significant concentration and are found to form 3-fold degenerate rotors that contribute to TLS loss throughout the GHz regime. These defects can be verified as a GHz TLS by measuring their concentration with infrared spectroscopy, similar to other oxides [68], and their role as a TLS studied with microwave absorption. A distribution of barrier heights due to the different possible defect charge states is predicted to range from 214 to 731 meV and corresponds to a TLS frequency range of 0.02 to 13 GHz. However, modulation of the Fermi level may provide a route for tuning the loss properties due to hydrogenated Al vacancies by changing the defect charge state and thus the TLS energy. Additionally, substitution of H with deuterium may offer another route for altering the loss properties due to hydrogenated defects by reducing their tunneling energies. The tunneling nature of the hydrogenated cation vacancy in alumina results from the localization of the H on the nearest neighbor O atoms. The creation of the off-center positions for H⁺ facilitates the high tunneling rate for this particular defect type and results from the weak interactions between neighboring O atoms and H⁺ positioned at the Al lattice site. *We expect this is a general trend for oxides* where the formation of hydrogenated cation vacancies, and the likelihood of these defects in other oxides has been demonstrated [69], creates a corresponding TLS.

From the computed range of viable formation energies shown in Figure 3.5 for a q=-2 hydrogenated Al vacancy, a formation energy of 0.5 eV is found to be reasonable for a slightly O-rich environment and a mid-gap Fermi energy. For an equilibrium temperature of 300C, this can easily lead to a defect concentration of 10^{18} /cm³. With the TLS asymmetry energy spread over a 100 MHz band and tunneling energy spread over a few orders of magnitude we find $P_0 \sim 3 \times 10^{45}/(\text{Jm}^3)$, where this result is only logarithmically sensitive to the range of tunneling energies. For the calculated dipole of 3 Debye, this results in a loss tangent on the order of tan $\delta \sim 2 \times 10^{-3}$, a value consistent with loss from large-area alumina Josephson junction barriers in qubits [35].

Interstitial H is found to form a 6-fold degenerate rotor in the q = +1 charge state with a plane of rotation parallel to the (0001) face that coincides with the S₆ inversion point of α -Al₂O₃. Analysis of the charge on the tunneling atom along the MEP confirms that the interstitial H is a proton and that the O-H interaction is ionic. The higher order degeneracy of this tunneling rotor leads to significant coupling between local minima and produces a TLS in the mid GHz energy range. Although these defects are only likely to occur at low Fermi levels and may be difficult to realize experimentally in crystalline alumina, they are predicted to create loss onset in the mid GHz regime and into the THz regime. The reduced forms of interstitial H defects, q = 0 and -1, do not create a rotor defect because the H is constrained to a single local minima equidistant from the six neighboring O atoms. For these charge states the ionic O-H interaction is no longer favorable and the nearest tunneling site is an equivalent defect site on a different set of neighboring O atoms with a barrier to tunneling > 1eV. Thus, the q = 0 and -1 charge states of interstitial H defects are predicted to not contribute to TLS loss at low temperatures.

3.2.5 Summary

The formation energy and low-temperature tunneling energies were calculated for bulk and surface hydrogen defects using *ab initio* methods. All defects were studied in alumina, a common dielectric in superconducting devices, and had a sufficient dipole moment to cause strong coupling to a superconducting qubit. We found that the interstitial H defect may cause a substantial loss with onset in the mid GHz regime and into the THz regime. Negatively-charged hydrogenated cation vacancies are found to likely form and have tunneling energies which are sufficiently low in frequency to cause loss throughout the GHz frequency range. This allows us to theoretically predict an important low temperature TLS for superconducting qubits, with a precise definition appropriate for amorphous and crystalline alumina. Hydrogenated cation vacancy defects should create TLS in other materials, as should various other defects which can be predicted by similar methods.

Chapter 4

Mechanism of Pseudocapacitance in MnO_2

4.1 Introduction

4.1.1 Pseudocapacitive Charge Storage

The promise of simultaneous high energy and power density in one device has sparked growing interest in electrochemical supercapacitors based on pseudocapacitive materials [70, 71]. The performance of electrochemical supercapacitors as compared to current battery technologies is shown in Figure 4.1. A possible route to increasing the energy densities of electrochemical supercapacitors is by utilizing pseudocapacitive charge storage materials. In addition to double-layer capacitance [72], pseudocapacitive materials are known to store charge at the surface and near-surface region through electrochemical charge transfer processes. Figure 4.2 depicts the ion intercalation leading to charge storage in the near-surface and bulk regions of a metal oxide pseudocapacitive material.



Figure 4.1: Specific power against specific energy (Ragone plot) of current electrochemical energy storage materials from Ref. [73].

Figure 4.2: Depiction of the ion intercalation process into the bulk and near-surface regions of a metal oxide pseudocapacitive material occuring at the solid-electrolyte interface. In addition to the double-layer capacitance, the intercalation of ions in pseudocapacitive materials results in additional capacitance from electrochemical charge transfer processes.

These charge transfer processes have been described as occurring at broadened equilibrium potentials that overlap to result in a nearly linear dependence of charge transferred (Q) versus applied potential (Φ), and thus a nearly constant capacitance $(C = \frac{dQ}{d\Phi})$ [74]. This electrochemical behavior mimics the rectangular-shaped cyclic voltammetry (CV) curves of double-layer or parallel-plate capacitors and is therefore termed "pseudocapacitance". Because pseudocapacitor electrodes based on manganese dioxide (MnO₂) exhibit a high experimental specific capacity and are composed of low toxicity earth-abundant elements, they have become an attractive choice for commercialization [73, 75, 76]. A depiction of the cation and proton reduction (shown in blue) and oxidation(shown in red) reactions that lead to the broadened equilibrium potentials and rectangular-shaped CV curves suggested for MnO_2 is shown in Figure 4.3 from ref. [73].

Figure 4.3: Illustration of the cation and proton reduction (shown in blue) and oxidation (shown in red) reactions that lead to the broadened equilibrium potentials and rectangular-shaped CV curves suggested for MnO_2 from ref. [73].

The operating conditions, including electrolyte type, and the complimentary anode material are important considerations for electrochemical capacitor performance. For example, an asymmetric supercapacitor composed of a MnO_2 cathode and a carbon anode operating in an aqueous medium provided a higher energy density and power density over a 2V operating potential than comparable symmetric carbon only based supercapacitors [77]. As depicted in Figure 4.4, design consideration was given to the stability window of the electrode materials and of the electrolyte to take advantage of the overpotentials required for H_2 reduction on carbon and O_2 oxidation on MnO_2 to extend the useful operating potential window of aqueous medium.

Figure 4.4 from ref. [77]: (left) Pourbaix type diagram depicting the overpotentials required for O_2 oxidation on α -MnO₂ and for H₂ reduction on activated carbon to extend the useful operating potential range for aqueous media. (right) Comparison of cyclic voltammetry for α -MnO₂ and activated carbon as the working electrodes demonstrating the complimentary capacitance features for increased performance.

Therefore, to understand the mechanism of pseudocapacitance, it is importance to identify the role of the band gap, work function, the point of zero charge, and the tunnel sizes of the electrode material, as well as the pH and stability window of the electrolyte in determining the charge storage abilities of a given electrode material.

4.1.2 Model Description

In this study, we reveal the fundamental basis for pseudocapacitance in MnO_2 . Our analysis is performed within a widely transferrable band diagram framework to evaluate the electrochemical processes of charge storage, as illustrated in Figure 4.5.

Figure 4.5: Band diagram and charge-switching alignment of an electrochemical supercapacitor electrode. (a) Simplified band diagram description of the electrode components. The electrode is composed of an electrically conducting current collector, an electrochemically active electrode material with a bulk band gap, E_{g} , and an electrolyte with a known stability window, outside of which it undergoes either oxidation or reduction. Electrochemically active electrodes possess defects with electronic energy levels within the band gap that undergo electrochemical reduction/oxidation to store charge. Consequently, we define these defect levels that lead to pseudocapacitance as "charge-switching states". The operating window is limited to the region of potentials where the electrode band gap and electrolyte stability window overlap. (b) Charge-switching states at potentials (E_n^0) are broadened by interactions with their surroundings resulting in a nearly linear relationship between potential and stored charge, and a constant capacity.

In this framework, defect-induced electronic levels within the band gap (chargeswitching states) store charge by accepting and donating electrons as the applied potential moves the Fermi level above and below their charge switching potentials, respectively. The role of charged defect states has been studied for a variety of applications [17, 78-80], however the approach we apply here to identify thermodynamicallv accessible charge-switching defect within states an electrochemical framework has previously not been used to study pseudocapacitance. Our approach evaluates the alignment of the potential at which charge-switching states accept or donate electrons with the scanned potential window (SPW) allowed by the electrolyte, beyond which the electrolyte undergoes oxidation or reduction. The equilibrium potentials (E^0) and thermodynamics of these charge-switching states are computed using quantum mechanical calculations employing density functional theory with a screened non-local exchange-correlation functional (HSE06) [26-28]; computational details are provided in the methods section 4.2. We use a bulk description to calculate defect states and incorporate the impact of the electrolyte to simulate the environment near the electrode surface. This framework identifies the importance of the band gap, work function, and point of zero charge of the electrode material, as well as the pH and stability window of the electrolyte as constraints on the viability of a given electrode material.

4.1.3 MnO₂ as a Pseudocapacitor

Until now, no detailed charge storage mechanism has been developed for MnO_2 pseudocapacitance. However, many experimental observations pertaining to the mechanism have been documented and any proposed mechanism must be

reconciled with these observations to be viable. Ex situ X-ray photoelectron spectroscopy (XPS) studies indicate that the charge storage process in aqueous electrolyte involves the formation and disappearance of hydroxyl groups on the electrode surface and a concomitant change in the formal oxidation state of Mn from 3^+ to 4^+ [73, 81]. Also, an observed pH dependence of pseudocapacitance suggests that processes mediated by protons account for ~1/2 of the specific capacity of MnO₂ [82, 83]. Other cations, in addition to protons, are also involved in charge storage and are thought to contribute the remaining capacity [73, 81, 82, 84]. Both protons and larger cations have been described to intercalate and deintercalate [84, 85] through bulk MnO₂ during charging and discharging [86]. These observed sources of charge storage have been combined to express the reactions involved in the pseudocapacitive charge storage of MnO₂ as [73, 81, 82, 84].

$$Mn_{(x+y)}^{(III)} Mn_{1-(x+y)}^{(IV)} OOM_x H_y \leftrightarrow Mn^{(IV)} O_2 + xM^+ + yH^+ + (x+y)e^-$$
(4.1)

where M^+ represents a singly charged cationic species. A similar expression describes reactions between MnO_2 and multiply charged cations involved in pseudocapacitance. The intercalation of Na into α -MnO₂ was found to occur spontaneously in the presence of a Na ion electrolyte and capacitance was significantly increased relative to pure α -MnO₂ [87], as shown in Figure 4.6, further demonstrating the importance of the role of cations in pseuodocapacitive charge storage.

Figure 4.6 from ref. [87]: Cyclic voltammograms of Na_xMnO_2 and α -MnO₂ electrodes, demonstrating the higher capacitance of the Na_xMnO_2 electrode.

The specific capacity of MnO_2 strongly depends on its film thickness and crystalline phase, with specific capacities reported for thin-film α -MnO₂ of ~1000 F/g and as high as 1380 F/g, which corresponds to 1.1 electrons per Mn center [81, 88]. In contrast, crystalline α -MnO₂ materials exhibit a bulk capacitance of only ~200 F/g, while β -MnO₂ has a meager bulk capacitance of ~10 F/g [89, 90]. One explanation given in the literature for the capacity differences between α -MnO₂ and β -MnO₂ is the tunnel (also called channel) sizes of their crystal structure; α -MnO₂ has larger tunnel sizes that have been suggested to enhance ion diffusion (e.g. proton conductivity) and provide additional adsorption sites to accept cations [81, 91, 92]. However, the pervasiveness of surface and bulk proton defects in metal oxides without tunnel structures [51, 80, 93] and the observed pseudocapacitance in crystal structures without tunnels, such as RuO_2 [73], suggests that the smaller tunnel size alone does not preclude β -MnO₂ from exhibiting pseudocapacitance. Our work identifies dramatic differences in the electronic properties of α -MnO₂ and β -MnO₂ and elucidates a detailed pseudocapacitance mechanism that explains the capacity difference between these crystalline phases, as well as the higher capacity of thin-film α -MnO₂.

4.2 Methods

4.2.1 Electronic Structure Calculations

Electronic structure calculations were performed using density functional theory (DFT) and the projector augmented-wave (PAW) [52, 53] method as implemented in the Vienna Ab initio Simulation Program (VASP) [53, 54, 94]. The chemically active hydrogen 1s, lithium 1s and 2s, sodium 2p and 3s, potassium 3p and 4s, oxygen 2s and 2p and manganese 3p, 4s and 3d electrons were described explicitly using PAWs while core electrons were described using pseudopotentials. In order to model the electronic structure in a manner consistent with electrochemical supercapacitor (ECSC) operating temperatures and with the experimental observation of Néel temperatures below 100K for both α - and β -MnO₂ [95-97], a constraint of low total spin was imposed by restricting calculations to spin configurations with low net spin.

To compensate for the self-interaction error introduced by semilocal exchange functionals in describing defects [24, 25] the Heyd-Scuseria-Ernzerhof hybrid exchange-correlation functional [26-28] was selected with a mixing parameter of 25% Hartree-Fock (exact) exchange (HSE06) and employing the standard range This fraction of exact exchange was determined by separation parameter. reproducing both the band-gap and band edge composition of β -MnO₂ described using partially self-consistent GW_0 quasiparticle calculations [29, 30] on the HSE wavefunction (HSE|GW₀), which have been shown to be reliable for determining band gaps of semiconductors and insulators [30]. The projected density of states for β -MnO₂ using HSE | GW₀ are shown in Figure 4.7. Because the Mn and O valence states are similar between the two phases of MnO_2 investigated, GW_0 quasiparticle calculations on only one phase are required to calibrate an HSE mixing parameter appropriate for describing both phases. The β -MnO₂ phase was selected for GW₀ benchmarking calculations because of its significantly smaller unit cell, and consequently more practical calculations.

The lattice parameters, band-gap, and formation enthalpy of β -MnO₂ predicted by HSE06 closely matched experimental values as presented in Table 4.1. In contrast, the Perdew, Burke and Ernzerhof exchange-correlation DFT functional with a 4 eV Hubbard on-site interaction term (PBE+U) failed to predict a band gap for β -MnO₂, consistent with previous PBE+U results that incorrectly predict that β -MnO₂ is metallic [23].

β -MnO ₂ Property	HSE06	HSE GW0	PBE+U	Measured
	4.34			4.40°
Lattice parameters a,b,c	191			4 40c
(Å)	4.04			4.40°
	2.83			2.88^{c}
Volume (Å ³)	53.71		59.32^{a}	55.48^{b}
E_{g} (eV)	1.6	1.7	0.0^{a}	1.0^{d}
	E 9		1 50	E 4h
$\Delta \mathbf{n}_{\mathrm{f}}(\mathrm{ev})$	-0.3		-4.0 ^a	-0.45

Table 4.1: Properties of β -MnO₂ calculated using HSE06, HSE06|GW0, and PBE+U compared to experimentally determined values.

^aRef. [23], ^bRef. [98], ^cRef. [99], ^dRef. [100]

Figure 4.7: Comparison of the projected density of states (PDOS) for β -MnO₂ calculated with HSE06 and GW₀. Calculated PDOS using (a) HSE06 and a 4×4×4 k-point mesh, (b) HSE06 | GW0 and a 4×4×4 k-point mesh, and (c) HSE06 using just the Γ -point. The total DOS (black) is decomposed by projecting the DOS onto the O[2p] (red) and Mn[3d] (blue) components of the density of states.

All bulk Mn, α -MnO₂, and β -MnO₂ and molecular O₂, H₂, H₂O, LiOH, NaOH and KOH calculations were spin polarized and performed using a 400 eV plane wave cutoff energy and computed to < 1 meV convergence. The bulk properties of α and β - MnO₂ were calculated using 12 and 6 atom unit cells with 3×3×3 and 4×4×4 evenly spaced Γ -centered k-point grids, respectively. All defect calculations were conducted sampling only the Γ -point of geometrically optimized 72-atom supercells, as illustrated in Figure 4.8 (with the defect site locations). As expected, Γ -point calculations reproduced results calculated using k-point expansions due to the extensive Brillouin zone folding inherent in relatively large supercells.

Figure 4.8: α -MnO₂ and β -MnO₂ supercells and corresponding defect locations. 3dimensional renderings and (001) view of 72-atom supercells of α -MnO₂ (a and b) and β -MnO₂ (c and d) indicating the locations of manganese vacancies (*V*_{Mn}) and

their cationated form (M_{Mn}), oxygen vacancies (V_O), and cation interstitial defects (${}^{2x2}M_i$ and ${}^{1x1}M_i$). ${}^{2x2}M_i$ cation interstitials reside in the larger 2×2 tunnels, whereas ${}^{1x1}M_i$ cations are situated in the smaller 1×1 tunnels.

Shown in Figure 4.9 are the PDOS of α - and β -MnO₂, evaluated at the Γ point. The calculated α -MnO₂ band gap (E_g) of 2.7 eV is only slightly larger than the reported 2.4 eV experimental band gap determined by photoluminescence [101]. Analysis of the calculated α -MnO₂ band structure (computed using a 3×3×3 k-point mesh) confirms the predicted minimum band gap to be indirect. The calculated β -MnO₂ direct band gap at the Γ -point of 1.6 eV (1.7 eV using HSE06|GW0) is also larger than the experimental value of 1.0 eV as measured using X-ray Absorption Near-Edge Structure (XANES) [100]. Although this discrepancy for β -MnO₂ will prove irrelevant to the mechanistic details of pseudocapacitance in β -MnO₂, we expect that our predicted band gap of 1.6 eV, which is consistent with previous hybrid DFT results that predict a band gap of 0.6 to 1.5 eV for β -MnO₂ [23], to be reliable. Furthermore, the composition of the band edges (O[2p] for the valence band maximum and Mn[3d] for the conduction band minimum) agrees with XANES results for β -MnO₂ [100].

Figure 4.9: PDOS of α - and β -MnO₂. Plots of the total DOS (black), with PDOS of Mn[3d] (blue) and O[2p] (red) orbitals for (a) α -MnO₂ and (b) β -MnO₂ at the Γ -point. The indirect band gap for α -MnO₂ (computed using a $3\times3\times3$ k-point mesh) and direct band for β -MnO₂ are indicated by the dashed lines.

4.2.2 Defect Formation Energies

Bulk defect formation energies (E_f) for a given defect and charge state were derived from total energy calculations performed using density functional theory with a screened non-local exchange-correlation functional (HSE06) [26-28]. This functional was calibrated to the results of quasiparticle band structure calculations performed using partially self-consistent GW₀ calculations [29, 30]. For a given
defect (D) in charge state q, E_f is expressed in terms of the chemical potentials μ_i of the defect atom (i) and electron (e) according to: $\Delta E_f(\mu_i, \mu_e) = E_{tot}^{D,q} - E_{tot}^P - \sum n_i \mu_i + q\mu_e$. Here, $E_{tot}^{D,q}$ and E_{tot}^P are the calculated total energies of the defective (D) and perfect (P) supercells, respectively, and n_i is the change in the number of atoms of *i* corresponding to the crystal defect [17]. The electron chemical potential μ_e is a function of the Fermi energy (ε_i) with respect to the valence band maximum energy (E_{VBM}) of the perfect crystal according to $\mu_e = \varepsilon_f + E_{VBM} + \Delta E_{loc}^H$. Finite-size effects and the compensating background charge of charged defect calculations were accounted for using the differences in average local Hartree potential (ΔE_{loc}^H) at a fixed plane far from the crystal defect to align the band structures [102].

The values of μ_i for each atomic species i are constrained by the stability relations of the constituent species necessary for the given phase to exist in equilibrium. For a manganese dioxide phase, μ_i values are bound by Mn-rich and O-rich conditions such that the stability relation $\mu_{Mn} + 2\mu_0 = \Delta H_f(MnO_2)$ is satisfied at these conditions. Here, $\Delta H_f(MnO_2)$ is determined from total energy calculations of the perfect crystalline MnO₂ phase of interest and constituent atoms in their reference states. The introduction of cation (M ϵ {H, Li, Na, K} in this study) interstitial or substitutional defects were accounted for by the addition of the stability relationships $\mu_M + \mu_H + \mu_0 = \Delta H_f(MOH)$, where again $\Delta H_f(MOH)$ is determined from total energy calculations of a molecule of MOH and the constituent atoms M, O and H in their reference states. These five stability equations contain six unknown chemical potentials (μ_H , μ_{Li} , μ_{Na} , μ_K , μ_O and μ_{Mn}). If any one of the unknown μ_i is specified, the μ_i of the other species are determined using the five stability relations.

The specific equilibrium conditions for which defect formation is relevant in many applications is typically undefined. Therefore, defect formation energies are reported within a range of physically meaningful bounds. In a metal oxide these bounds are limits imposed by the elemental reference states resulting in metal-rich (oxygen-poor) or oxygen-rich (metal-poor) conditions under the constraint that the stability relations are satisfied. In this work, equilibrium experimental conditions are used to define the μ_i to predict ΔE_f relevant to electrochemical supercapacitor (ECSC) operating conditions. The defect formation energies of interstitial and substitutional defects in α - and β -MnO₂ for Mn-rich and O-rich conditions are reported in Figure 4.10.



Figure 4.10: Mn-rich and O-rich defect formation energies. Defect formation energies (ΔE_f) versus Fermi level (ε_f) for α -MnO₂ (a and b) and β -MnO₂ (c and d) under Mn-rich (a and c), where $\mu_{Mn} = \Delta H_f(Mn_{fcc})$, and O-rich (b and d), where $\mu_0 = \frac{1}{2}(\Delta H_f(O_2))$, conditions for all α - and β -MnO₂ defects studied in this work. It should be noted that the charge-switching potentials are equal for Mn-rich, O-rich, and the applied bias (pH/ Φ) defined chemical potentials, and that the reported formation energies are only valid within the band gap of each material. The reference compositions (bounds) chosen to define the chemical potentials of all species in the system only impact the formation energies.

4.2.3 Chemical Potential of H at the Experimental pH and Applied Bias

The value of μ_H is specified in this work according to the H₂/H⁺ equilibrium relationship under an applied bias as $\mu_H = \frac{1}{2}\mu_{H_2} = \mu_{H^+} + \mu_e^0 - + e\Phi$. Here, Φ is the applied bias versus a reference, e is a positive elementary charge, $\mu_{e^-}^0$ is the chemical potential of an electron at the reference potential, and μ_{H^+} is the chemical potential of the proton, which we approximate from the experimental pH by taking $\mu_{H^+} \cong -0.059(pH)$ [103]. For aqueous MnO₂ electrochemical supercapacitors, Φ is commonly scanned from 0.0 to 1.0 V relative to a Ag/AgCl reference electrode. For this work, we reference Φ to Ag/AgCl by taking the potential of the Standard Hydrogen Electrode (SHE) versus vacuum as 4.44 V [104, 105] and Ag/AgCl vs. SHE as 0.197 V [103], yielding a value of $\mu_e^0 = -4.637 \, eV$. Additionally, the dissolved salt used in aqueous MnO₂ ECSCs is typically a weak base such as KCl or Na_2SO_4 at concentrations ≤ 1 M. Therefore, a slightly basic pH of 7.4 arising from the 0.1 M Na₂SO₄ aqueous electrolyte commonly employed for MnO₂ ECSC systems [89, 106] was used to specify $\mu_{H^+} \cong -0.44 \ eV$.

Inserting the experimentally defined values of $\mu_{e^-}^0$ and μ_{H^+} into the H₂/H⁺ equilibrium relationship with an applied bias results in a linear dependence of μ_H on applied potential ($\mu_H \propto \Phi$). Furthermore, Φ can be directly related to ε_f , such that $\Delta E_f(\mu_H, \mu_e) = Constant + \varepsilon_f(q + 1)$. As a result, the inclusion of an applied potential Φ into the calculation of μ_H results in an integer shift in the slope of ΔE_f vs. ε_f for each change in charge state q (Section 4.2.4). This approach differs from previous defect formation studies where ΔE_f are plotted as a function of ε_f for a set of fixed μ_i ; here μ_H as a function of Φ is included in the stability relations to enable calculation of equilibrium defect formation energies ΔE_f of an electrode material at electrochemical operating conditions.

4.2.4 pH Derived Chemical Potentials of All Species

Using the relationship $e\Phi = \mu_e^0 + W - \varepsilon_f$, (Section 4.2.5), an expression for μ_H in terms of ε_f can be written as:

$$\mu_H(\varepsilon_f) = \mu_{H^+} + 2\mu_{e^-}^0 + W - \varepsilon_f \quad (4.2)$$

where μ_{H+} , μ_e^{0-} , and W are all constant for a given system such that ε_f is the only variable in this expression for μ_H . i.e. $\mu_H = K_0 - \varepsilon_f$, where $K_0 = \mu_{H+} + 2\mu_e^{0-} + W$. Substituting this into the defect formation energy equation, $\Delta E_f(\mu_i, \mu_e) = E_{tot}^{D,q} - E_{tot}^P - \sum n_i \mu_i + q \mu_e$, with a single interstitial hydrogen $(n_H=1)$, and substituting $\mu_e = \varepsilon_f + E_{VBM} + \Delta E_{loc}^H$ (Section 4.2.2), the expression for $\mu_H = f(\varepsilon_f)$ yields:

$$\Delta E_f(\varepsilon_f, q) = E_{tot}^{D,q} - E_{tot}^P - K_0 + q(E_{VBM} + \Delta E_{loc}^H) + \varepsilon_f(q+1) \quad (4.3)$$

where the slope of ΔE_f vs. ε_f is equal to (q+1).

Using the expression for μ_H as presented in 4.2.3, the chemical potential of oxygen is found to be:

$$\mu_0(\varepsilon_f) = \Delta H_f(H_2 O) - 2\mu_H = \Delta H_f(H_2 O) - 2K_0 + 2\varepsilon_f \quad (4.4)$$

such that with a single oxygen vacancy (no=-1), the slope of ΔE_f vs. ϵ_f is equal to (q+2).

Using this expression for μ_0 and the formation energy of MnO₂, the chemical potential of manganese is found to be:

$$\mu_{Mn}(\varepsilon_f) = \Delta H_f(MnO_2) - 2\mu_0 = \Delta H_f(MnO_2) - 2\Delta H_f(H_2O) + 4K_0 - 4\varepsilon_f \quad (4.5)$$

such that with a single manganese vacancy (n_{Mn} =-1), the slope of ΔE_f vs. ϵ_f is equal to (q-4).

Furthermore, using the derived expressions for μ_0 and μ_H , the chemical potential of the remaining interstitial cations is found to be:

$$\mu_M(\varepsilon_f) = \Delta H_f(MOH) - \mu_O - \mu_H = \Delta H_f(MOH) - \Delta H_f(H_2O) + K_0 - \varepsilon_f \quad (4.6)$$

such that with a single interstitial cation ($n_{Mi}=1$), the slope of ΔE_f vs. ϵ_f is equal to (q+1).

4.2.5 Work Functions and Potential of Zero Charge Corrections

In order to reference the band gaps of bulk crystalline α - and β - MnO₂ to the scanned potential window, the work functions (W) of these crystalline materials must be determined. We calculated the work functions of α - and β - MnO₂ using the electrostatic local potential following the method of Fall *et al* [107]. The change in the local electrostatic potential between the material slab and vacuum (ΔV_{el}) was determined by performing 72-atom unrelaxed slab calculations, while ε_f^0 was calculated with respect to the average local electrostatic potential using bulk unit cell calculations. The work function of bulk materials is known to depend on the surface termination due to the influence of the electric fields created by surface dipoles of various strengths for different terminations. For this work, the thermodynamically favorable close-packed (110) surfaces were used to determine the work functions for both α - and β - MnO₂ [108, 109]. When interface conditions produce a net surface charge density, the potentials of the band edges at the surface shift relative to the Potential of Zero Charge (PZC), resulting in a bending of the electronic bands. When the net surface charge is produced by acid-base conditions, such as at the experimental pH of 7.4 common in MnO_2 ECSCs, the band edge shifts can be determined from the Nernstian relationship.

$$V = V_{PZC} + 0.059(pH_{PZC} - pH)$$
(4.7)

We set the value of pH_{PZC} to 7.3 for pyrolusite (natural β -MnO₂) and 1.7 for cryptomelane (α -MnO₂ with potassium doping) to evaluate the band bending corrections [100, 110, 111].

The plane-averaged electrostatic local potential as a function of depth for the 72-atom supercell slab model of the (110) surface of α -MnO₂ and β -MnO₂ is shown in Figure 4.11. From this data, we determined the work function W for the (110) surface of α -MnO₂ to be 8.0 eV and W to be 8.1 eV for β -MnO₂. After PZC corrections for an experimental pH of 7.4, α -MnO₂ and β -MnO₂ (110) surfaces are predicted to have work functions of 7.7 eV and 8.1 eV, respectively.



Figure 4.11: Work function derived from electrostatic potential. Electrostatic potential versus depth for a (110) frozen slab (black) and bulk (red) supercell of (a) α -MnO₂ and (b) β -MnO₂ with the positions of the MnO₂ (110) atomic planes marked by purple circles. Note that the bulk and slab plane averaged potentials are in close agreement within the slab. The work function W, which is the difference between the vacuum energy and the surface VBM is illustrated.

4.2.6 Derivation of the energy of formation (E_f) versus Fermi energy (ε_f)

In Figure 4.12, the Fermi energy ε_f with respect to the valence band maximum (VBM) is shown as determined by the applied potential relative to an electrochemical reference (Φ). From this figure, it can be seen that

$$e\Phi = \mu_e^0 + W - \varepsilon_f \qquad (4.8)$$

where μ_{e}^{0} is the Fermi energy of the electrochemical reference and W is the work function of the electrode material in question.



Figure 4.12: Band diagram relationship between Φ and $\varepsilon_{\rm f}$. This band diagram shows the relationships between the applied bias (Φ) and resulting Fermi energy in relation to the valence band maximum energy (VBM), work function (W) and the energy of the reference potential μ_e^0 -. Note that a more positive applied potential Φ results in a lower Fermi energy.

4.2.7 Complete Defect Formation Diagrams at pH 7.4

A plot of the defect formation energies versus Fermi energy at pH of 7.4 and under an applied bias for all defects studied in α -MnO₂ are shown in Figure 4.13. This figure shows the range of thermodynamic stability of defects of various charge state as well as the predicted transitions between the charge states of the defects, including those not explored within the main text and which are secondary to the explanation of charge storage mechanism in α -MnO₂.



Figure 4.13: Comprehensive pH-derived defect formation energies. Defect formation energy diagrams for all the defects studied in α -MnO₂ (a) and β -MnO₂ (b) at a pH of 7.4 and under an applied bias. The scanned potential window from 0.0 to 1.0 V relative to a Ag/AgCl reference electrode is shown in the shaded region.

4.2.8 Theoretical Capacity of MnO_2 Based on 1 e⁻ Transfer per Mn Atom

The maximum theoretical specific capacity of MnO_2 has been assumed in previous work to be limited to one electron per manganese center, and capacities corresponding to ~1.1 electrons per manganese center have been verified experimentally for thin-film manganese dioxide [73, 81]. Assuming a transfer of one electron per formula unit, $(1e/MnO_2)$, this yields a maximum theoretical capacity for α-MnO₂ of 1233 F/g for a 0.9 V potential window and 1110 F/g for a 1.0 V potential window. The number of bulk cation sites available per a-MnO₂ formula unit identified in our work is $0.25 \ ^{2x2}M_i$ and $0.5 \ ^{1x1}H_i$, where each $\ ^{2x2}M_i$ and $\ ^{1x1}H_i$ contributes two charge-switching states. A simple addition of these effects yields that the total number of states available per MnO_2 unit is 1.5, plus a small contribution from any manganese vacancies. This suggests that ~ 1.5 electrons could be stored per manganese center for bulk α -MnO₂—higher than the maximum theoretical capacity of assuming 1 electron per manganese center. This means that for a 1 V potential window, the maximum predicted capacity based on the mechanism in this work is 1665 F/g-50% higher than the 1110 F/g one would calculate assuming one electron per manganese center for the same potential window. However, the treatment used in this work assumes non-interacting defects, and uses a surface description for the location of band edges. With defect interactions, the formation energies and charge-switching potentials are expected to change with respect to the non-interacting picture. Additionally, if more than one electron is transferred per manganese center, the resulting unstable Mn^{2+} centers are expected to increase dissolution of the MnO_2 [112, 113]. Furthermore, the effect of band-bending is diminished farther into the bulk and the number of chargeswitching states within the scanned window is expected to decrease. Therefore, realizing the theoretical specific capacity of 1665F/g of thin-film α -MnO₂ over a 1 V potential window predicted by our cation-mediated mechanism will be limited by defect interactions and practical considerations of material stability.

4.3 Cation Mediated Pseudocapacitance

4.3.1 Calculated Band Alignment Constraints in MnO₂

The band alignments for α - and β -MnO₂ are plotted on an absolute scale with respect to an electron in vacuum in Figure 4.14. The alignments were determined using calculated pH-corrected work functions of 7.7 and 8.1 eV for the (110) surfaces and a calculated indirect band gap of 2.7 eV and a direct band gap of 1.6 eV for α and β -MnO₂, respectively. The SPW within the allowed aqueous electrolyte window is also displayed for comparison. This analysis shows that the experimental SPW (0 to 1 V vs. Ag/AgCl) [112, 113] does not overlap with the band gap of β -MnO₂. For a β -MnO₂ electrode, the SPW is entirely in the conduction band, so the potential at a β -MnO₂ electrode will simply be pinned in the conduction band over the SPW and the charge-switching states in β -MnO₂ will not switch charge at experimentally accessible potentials. Thus, β -MnO₂ is not an effective charge storage material in aqueous electrolyte, as observed experimentally. In contrast, the band gap of α -MnO₂ overlaps with the SPW. Therefore, α -MnO₂ will be a viable pseudocapacitor material if its charge-switching states lie within the portion of its band gap that overlaps the SPW of the electrolyte, and its charge-switching state are thermodynamically favorable.



Figure 4.14: Band diagram alignment. The absolute band edge energies of α -MnO₂ (left) and β -MnO₂ (center) and the electrochemical potential window scanned for aqueous MnO₂ at pH = 7.4 (right).

4.3.2 Charge Storage States

The possible charge-switching defect sites we investigate that may act as pseudocapacitive charge storage states in MnO_2 are depicted in Figure 4.15a. α - MnO_2 possesses both small 1×1 and larger 2×2 tunnels, whereas the β -MnO₂ structure only exhibits the smaller 1×1 tunnels (tunnel sizes are in units of Mn octahedral blocks). The views in the [001] directions show the locations of manganese vacancies (V_{Mn}) and their cationated form (M_{Mn}), which are Mn vacancies occupied by an M⁺ cation. In addition, Figure 4.15a also illustrates oxygen vacancy (V_0) and cation interstitial ($^{2\times2}M_i$ and $^{1\times1}M_i$) defects. The $^{2\times2}M_i$ interstitial cations are located in the larger 2×2 tunnels, whereas $^{1\times1}M_i$ cations are positioned in the smaller 1×1 tunnels. These defects may all potentially store charge and thus contribute to pseudocapacitance if they undergo charge-switching at potentials within both the band gap and the SPW of the electrolyte.





Figure 4.15: Cation induced charge-switching states of α -MnO₂ and β -MnO₂. (a) Crystal structures and defect sites of α -MnO₂ and β -MnO₂ with manganese atoms shown in blue and oxygen atoms shown in red. Results for (b) α -MnO₂ and (c) β -MnO₂ showing defect formation energies, ΔE_f , and location of charge-switching potentials as a function of applied bias, Φ . Charge-switching potentials are the potentials at which interstitial and substitutional cation defects undergo reduction/oxidation. The band gaps are indicated by the dashed vertical lines and the projected density of states (PDOS) for the negatively charged interstitial proton defects are shown in the bottom panel.

A comprehensive electrochemical thermodynamic picture for the calculated defects in thin-film α -MnO₂ at a simulated pH of 7.4 [89, 106] is shown in the defect formation energy plot in Figure 4.15b. Defects with a particular charge become thermodynamically favorable when their defect formation energies ($\Delta E_{\rm f}$) are less than zero. The potentials marked in Figure 4.15b indicate the potentials at which it is thermodynamically favorable for defects to accept an additional electron and therefore act as charge-switching states and store charge. By scanning the voltage to more reducing potentials (from left to right), an electron is transferred to the state at each point marked on the line, provided that the defect is present. Because the potential is pinned at the valence band and conduction band edges, the defect formation energies are not plotted beyond the band gap. The accuracy of the predicted charge-switching model is corroborated by multiple experimental observations. We show that protons will occupy Mn vacancies, creating Ruetschitype defects [114]. We also predict a stable potential window similar to the experimental potential window of $0 < \Phi < 1.0$ V vs. a Ag/AgCl reference electrode [112, 113]. Mn vacancies become favorable at $\Phi < 0.1$, and O vacancies become favorable at $\Phi > 0.8$. Only interstitial proton defects (1×1*H* and 2×2*H*) and protonated Mn vacancies (H_{Mn}) undergo charge-switching at potentials within the SPW of the electrolyte, indicating that these are the defects that lead to charge storage.

The calculated density of states (DOS), band gap and the SPW allowed by the aqueous electrolyte are also displayed for reference for α -MnO₂ in Figure 4.15b. Thindirect band gap of α -MnO₂ overlaps with the SPW and also contains charge-switching states within the SPW. In contrast, our calculations show that the charge-switching states that lie within the band gap of β -MnO₂ are outside the SPW (see Figure 4.15c). This analysis extends beyond examining the tunnel sizes of each phase and more accurately explains the pseudocapacitive properties of each material. These results demonstrate why α -MnO₂ is a viable pseudocapacitor material and why β -MnO₂ does not effectively store charge in aqueous electrolyte, as observed experimentally.

4.3.3 Dominant Interstitial Cation Mechanism in α-MnO₂

The dominant mechanism of charge storage in α -MnO₂ results from interstitial cations as illustrated in Figure 4.16a. First, an interstitial proton or cation, M⁺, localizes near an oxygen atom. The Coulombic field of M⁺ distorts the electronic distribution of the adjacent Mn-O bond, which stabilizes the corresponding Mn-O antibonding d-p π^* orbitals from the conduction band into the band gap. The projected DOS (PDOS) (Figure 4.16b) shows that these Mn-O antibonding states are primarily composed of Mn[3d] orbitals, which agrees with XPS results that indicate a change in the Mn valency from 4⁺ to 3⁺ over the SPW [81]. Applying a potential bias to the electrode populates or depopulates these stabilized antibonding orbitals leading to charge-switching of these interstitial defects. For thin-film α -MnO₂ at a pH of 7.4, Li⁺, Na⁺ and K⁺ have favorable interstitial formation energies for the ^{2×2} M_i site, whereas formation of interstitial H⁺ is favorable for both the ^{1×1} M_i and ^{2×2} M_i sites (Figure 4.16b). The favorable intercalation of larger cations into the 2×2 tunnels of α -MnO₂ is corroborated by the natural existence of cryptomelane and the spontaneous intercalation of Na⁺ into α -MnO₂ as observed experimentally [87]. These interstitial defects also all have charge-switching transitions that occur within the SPW, and should therefore all contribute to charge storage in α -MnO₂.







Figure 4.16: Interstitial and substitutional cation induced charge-switching states and their mechanism in α -MnO₂. (a) Illustration of the mechanism by which interstitial (top) and substitutional (bottom) cations create charge-switching states in α -MnO₂. Formation energy and charge-switching state alignments versus potential for (b) cations in the 2x2 tunnel and (c) Mn vacancies in α -MnO₂. The charge-switching states within the band gap are marked for defects associated with Mn (blue), H (black), Li (green), Na (purple) and K (orange). The states within the scanned potential window consist of interstitial cation defects and cationated Mn vacancies. The dominant orbital character of the states is denoted by the colored arrows in the PDOS shown in the lower panel.

4.3.4 Secondary Substitutional Defect Mechanism

A secondary mechanism for charge storage in a-MnO₂ results from cation substitution at Mn vacancies, as illustrated in Figure 4.16a. Removing a Mn atom to form a Mn vacancy eliminates interactions between the Mn and neighboring oxygen atoms and creates non-bonding O[2p] orbitals that are destabilized from the valance band into the band gap. For thin-film α -MnO₂ at a pH of 7.4, H⁺, Li⁺, Na⁺ and K⁺ all form cationated Mn vacancies that act as charge-switching states within the SPW, as shown in Figure 4.16c. When a cation occupies the Mn vacancy, a substitutional defect results with a more negative formation energy than the corresponding Mn vacancy. The substitutional cation interacts with the nonbonding O[2p] orbitals that resulted from formation of the vacancy to stabilize them, shifting them towards the valence band. The substitutional cation also interacts with Mn-O antibonding states to stabilize them and shift them from the conduction band into the band gap, as shown in Figure 4.16c. This effect is analogous to the stabilization of Mn-O antibonding states by interstitial cations in the $2 \times 2M_i$ sites. The radius of the 6-fold coordinated Mn⁴⁺ center removed to form the vacancy is ~0.5 Å [58]. Consequently, Li⁺ with a radius of 0.6 Å occupies this vacancy more favorably over the SPW than the larger cations we studied. For more oxidizing conditions our calculations predict that up to four protons will preferentially occupy Mn vacancies creating Ruetschi-type defects [114]. This suggests that a cation exchange process, if kinetically accessible, may also be active over the SPW for substitutional defects. However, the formation of cationated Mn vacancies requires the removal of a subsurface Mn atom, and the dissolution of Mn²⁺ within the scanned potential window. This process is expected to require a large kinetic barrier that limits the number of these states and consequently reduces their contribution to charge storage.

4.3.5 Cation Size Effects

While Li⁺, Na⁺, and K⁺ all result in ^{2×2} M_i defects with similar electronic character, alkali metal cations larger than Na⁺ are sterically hindered within the 2×2 tunnels of α -MnO₂ (Figure 4.17a). This analysis was performed using the ionic radii of 4-fold coordinated cations [58] with the ionic radius of a proton taken to be zero. The maximum passable ionic radius r_{max} is estimated using the calculated diagonal oxygen-to-oxygen distance in the 2×2 tunnel (D₀₀ = 5.01 Å) and the ionic radius for O² (r₀ = 1.21 Å) [58]. r_{max} for a 2×2 tunnel was then found to be ^{2×2}r_{max} = $\frac{1}{2}$ (D₀₀ - 2r₀) = 1.30 Å. Figure 4.17b shows the effect of the cation species on the formation energy of its interstitial defect. The ionic radius of K⁺ is larger than r_{max} and so the formation energy of ^{2×2}K_i is greater than the formation energy of ^{2×2}Na_i, as Na⁺ is slightly smaller than r_{max}.

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Figure 4.17: Effect of cation size in 2×2 tunnels of α -MnO₂. (a) Illustration of the parameters used in analyzing cation size effects. (b) Effect of the cation species on the formation energy of its interstitial defect. (c) Distance between the coordinated cation and the center of the 2×2 tunnel. (d) The energy of the most positive charge-

switching state for a given interstitial cation plotted relative to the energy of the valence band maximum (VBM).

The distance d between the coordinated cation and the center of the 2×2 tunnel is shown in Figure 4.17c. Of the 2×2 interstitial cations, H⁺ and Li⁺ are located close to the tunnel wall, whereas Na⁺ and K⁺ localize near the center of the tunnel and interact more equally with the neighboring oxygen atoms. The chargeswitching potential of the most positive charge-switching state for a given interstitial cation is plotted relative to the energy of the valence band maximum in Figure 4.17d. For example, the Na⁺ interstitial defect has an electrochemical potential for charge-switching at 2.1 V vs. EVBM or ~0.9V vs Ag/AgCl. As the electrode is scanned past this potential our calculations show that the interstitial Na⁺ induced gap states change charge state. All four cation interstitial defects have different charge-switching potentials resulting from their dissimilar formation energies and their interactions with the neighboring oxygen atoms in the tunnel walls, resulting in capacity differences for different cations as observed experimentally [82, 83, 86, 115]. A Na⁺ interstitial has the most favorable formation energy in the 2×2 tunnels of α -MnO₂.

An analogous pseudocapacitance mechanism is predicted for the ${}^{1\times1}M_i$ site where an interstitial cation induces a charge-switching state that undergoes electrochemical reduction to store charge. However, because ${}^{1\times1}r_{max}$ is only 0.40 Å, protons are the only singly charged cation small enough to occupy ${}^{1\times1}M_i$ sites. Therefore, only interstitial H⁺ contributes to charge storage in the 1×1 tunnels. This is corroborated by experimental observations that indicate that both protons and larger cations contribute to charge storage where roughly half of the capacity originates from protons [73, 81, 83]. We calculate that reduction of $^{1\times1}$ H⁺ interstitial defects occurs at 0.8 and 0.9 V vs Ag/AgCl. Thus, our calculations predict that as the potential is scanned past these two electrochemical potentials, the proton defect changes charge state by undergoing two discrete one electron reductions, in agreement with XPS results showing the dissociation and formation of hydroxyl groups [81].

4.3.6 High Capacity and Rate in α -MnO₂

The mechanism of pseudocapacitance based on the electrochemical reduction of interstitial and substitutional cation defects described above for α -MnO₂ at a pH of 7.4 predicts a high charge storage capacity arising from multiple chargeswitching states within the SPW and a high charge-discharge rate. The interstitial and substitutional mechanisms we identify as leading to charge storage are supported by the large observed capacity of cryptomelane (KMn₈O₁₆) [116, 117] and the enhanced capacity of α -MnO₂ when pre-intercalated with large amounts of Na⁺ [87]. In the limit of non-interacting defects and thin-film α -MnO₂, the interstitial cation mechanism shown in Figure 4.16a will result in 1.5 electrons transferred per Mn-center (Section 4.2.8), with a small additional contribution from the substitutional cation mechanism, also shown in Figure 4.16a. This accounts for the 1.1 electrons per Mn center observed experimentally for thin-film α -MnO₂ [81]. For the interstitial cation mediated mechanism, our calculations predict no kinetic limitation arising from ion transport through the electrode because protons and larger cations will favorably reside in 1×1 and 2×2 tunnels regardless of the applied potential, as shown in Figure 4b. The prediction that ion transport causes no kinetic limitation conflicts with previous descriptions of the pseudocapacitance mechanism that involve the transport of ions across the double-layer during charge and discharge [84-86, 118]. However, our assertion that the majority of charge storage capacity exhibited in these materials does not involve ion transport through the bulk electrode or across the double-layer agrees with the high rate of chargedischarge achievable by MnO_2 electrodes [84, 86, 88]. Furthermore, the secondary mechanism for charge storage based on substitutional cations (Figure 4.16a) does involve ion transport across the double-layer as the defect formation energies transition between being favorable and unfavorable over the SPW (Figure 4.16c). We predict that the majority of the capacity arises from interstitial cation defects and is thus not mass-transport limited.

4.3.7 Broadening of Peaks Leads to Rectangular CV

The calculated band diagram and predicted charge-switching defect states of α -MnO₂ are shown in Figure 4.18a. This analysis follows the framework presented in Figure 4.5. As an α -MnO₂ electrode is scanned from 0 to 1 V versus Ag/AgCl, each charge-switching state appears as a peak on the CV scan.





b

Figure 4.18: Effect of operating conditions on α -MnO₂ charge storage. (a) Quantitative band-diagram description of pseudocapacitive α -MnO₂ in aqueous electrolyte at a pH of 7.4 (b) Calculated Pourbaix diagram demonstrating the effects of pH on the band alignment and charge-switching potentials of defect states in α -MnO₂ relative to the scanned potential window and the pH dependence of interstitial and substitutional defect formation energies in α -MnO₂.

Similarly, the electrons involved in reducing or oxidizing the state appear as current at the applied electrochemical potential in a chronopotentiogram. The charge-switching states that switch charge at potentials within the SPW are the states that contribute to pseudocapacitance. However, we expect that the potential at which each charge-switching state undergoes reduction or oxidation shifts depending on the effects of its specific environment. For example, the chargeswitching potential will shift as a result of interactions with the solvent and other nearby adsorbed species or defects. Furthermore, the potential at which states change charge will also shift as a function of distance from the surface due to the interfacial field that gives rise to "band bending." These and other effects of the surroundings of the defects broaden their charge-switching potentials into a distribution spread about each reduction potential, E^0 . Both the distribution of the equilibrium potentials of the available states and their broadening due to band bending lead to a more rectangular CV — the quintessential feature of a pseudocapacitive material.

4.3.8 Consideration of Electrolyte and Operating Conditions

The effect of electrochemical operating conditions on the charge storage mechanism in α -MnO₂ pseudocapacitors is shown in Figure 4.18b. The top figure in Figure 4.18b is similar to a Pourbaix diagram and shows the electrolyte pH (i.e. $\alpha_{\rm H}^+$) sensitivity of the band alignments, charge-switching potentials and stability of MnO₂ with respect to the SPW. We find that the operating conditions must be thoroughly considered for optimal pseudocapacitor design and performance. For α -MnO₂, the pH and scanned window that produce the largest capacity in an aqueous electrolyte have been empirically determined, and result in a large capacity contribution from the surface and near-surface where band-bending occurs, and a smaller (but non-zero) capacity contribution from the bulk.

The effect of the electrochemical operating conditions on pseudocapacitance in α -MnO₂ predicted by our charge storage mechanism explains the higher observed capacitance for thin film α -MnO₂ relative to bulk α -MnO₂ [81, 89]. A pH near 7.4 favors MnO₂ stability and produces better alignment of the surface and near-surface α -MnO₂ band gap that facilitates cycling over a larger fraction of the distribution of charge-switching potentials. In contrast, at a pH of 1.7, the pH_{PZC} value for α -MnO₂, the allowed potential cycles into the equilibrium region for forming Mn²⁺ and has minimal overlap with either the band gap or charge-switching potentials. This potential of zero charge (PZC) pH condition corresponds to the flat band potential of bulk α -MnO₂ and indicates that the contribution to capacitance from bulk α -MnO₂ is limited relative to thin film α -MnO₂ capacities under optimal conditions.

Our calculations predict that the heats of formation are also sensitive to pH such that the concentrations of the different defects can be thermodynamically tuned in consideration of the electrochemical operating conditions (Figure 4.18b). We stress that the analysis contained in Figure 4.18 can be performed on any pseudocapacitive material to determine the optimal electrochemical operating conditions that maximize the density of charge-switching states within the SPW while maintaining material stability during cycling. For instance, if a non-aqueous electrolyte with a larger stability window and lower oxidation potential, and an appropriate proton activity were used, the proton-induced charge-switching states of β -MnO₂ could be made electrochemically accessible at potentials within the overlap of the band gap and electrolyte window.

4.3.9 Insights for Material and Electrolyte Selection

Our pseudocapacitance model and defect analysis identifies mechanisms by which a) interstitial cations induce charge-switching states in α -MnO₂ through stabilization of Mn-O antibonding orbitals from the α -MnO₂ conduction band and b) cations stabilize high energy dangling O[2p] bonds from the valence band resulting from Mn vacancies. Within the limitations of our approach, these mechanisms will result in 1.5 electrons transferred per Mn-center, which accounts for experimentally observed charge storage of up to 1.1 e-/Mn.

The charge-switching of these ion-induced band gap states as a mechanism to store charge should be generally applicable to other pseudocapacitance materials. For example, other multivalent metal oxides may incorporate interstitial cations that form charge-switching states through stabilization of M-O antibonding orbitals from the conduction band that localize in the band gap. We expect that the multivalent character of the metal center accommodates the localization of charge in these antibonding states leading to their stabilization into the band gap. Additionally, other metal oxides may also contain substitutional cations that interact with high energy O[2p] dangling bonds created by metal center vacancies to form charge-switching states in the band gap. We anticipate that materials could also be developed in which anions shift valence-band states into the band gap by a similar mechanism. If these charge-switching states overlap with the SPW allowed by the electrolyte, those materials will store charge by an analogous mechanism to the one proposed here for α -MnO₂.

4.3.10 Summary

In this work, we have identified an array of physical properties for electrode materials and electrolytes which work together to determine the viability of a material to store charge via pseudocapacitance. These include band gap, work
function, the point of zero charge, and the tunnel sizes of the electrode material, as well as the pH and stability window of the electrolyte. Our results predict that materials with band gaps that overlap with a given electrolyte window and that have thermodynamically accessible charge-switching defects are good candidates as pseudocapacitive materials. The band edge alignment of many materials with respect to the aqueous electrolyte window have been studied for applications in photoelectrochemical water splitting, and several have been identified as having poor water splitting abilities due to the presence of mid-gap states [119]. We suggest that these poor water splitting materials may be ideal for pseudocapacitive charge storage if these gap states lie within the SPW of the electrolyte. In general, the theoretical model for studying pseudocapacitive mechanisms developed and applied in this work should be applicable to the discovery and optimization of new Using the framework we have employed here for pseudocapacitive materials. MnO₂, computational materials screening can be employed to rapidly downselect and identify viable new pseudocapacitive materials, in line with efforts already in place to computationally identify materials for other electrochemical applications [8, 120-122].

Chapter 5

Conclusions

5.1 Summary of Key Results

We have demonstrated that the accurate prediction of materials properties and atomistic mechanisms, although still a significant challenge in condensed matter theory and computation, can be performed reliably by *ab initio* methods. Specifically, we computationally investigated defects in metal oxides that are relevant to dissipation loss in quantum computing materials and pseudocapacitance in charge storage materials.

In chapter 3, we performed *ab initio* calculations of hydrogen-based tunneling defects in Al_2O_3 , a common dielectric in superconducting devices, to identify deleterious two-level systems (TLS) in superconducting qubits. The formation energies were calculated for bulk and surface hydrogen defects, and the analogous deuterium defects, and provided us with an estimate of the likelihood of defect occurrence during growth. We also identified which defects had an appropriate TLS

energy corresponding to frequency for photon absorption in the GHz regime and had a sufficient dipole moment to cause strong coupling to a superconducting qubit. We found that the interstitial hydrogen defects should cause a substantial loss with onset in the mid GHz regime and into the THz regime. More importantly to superconducting qubit devices, we predicted that negatively-charged hydrogenated cation vacancies are found to likely form and have tunneling energies which are sufficiently low in frequency to cause loss throughout the GHz frequency range. This allowed us to theoretically predict an important low temperature TLS for superconducting qubits, with a precise definition appropriate for amorphous and crystalline alumina. We expect hydrogenated cation vacancy defects should create TLS in other oxides and materials, as should various other defects which can be predicted by similar methods.

In chapter 4, using first principles, we derived a detailed pseudocapacitive charge storage mechanism of MnO_2 and predicted the effect of operating conditions on charge storage using a combined theoretical electrochemical and band structure analysis. We identified the importance of the band gap, work function, the point of zero charge, and the tunnel sizes of the electrode material, as well as the pH and stability window of the electrolyte in determining the charge storage viability of a given electrode material. We found that high capacity of α -MnO₂ results from cation induced charge-switching states in the band gap that overlap with the scanned potential allowed by the electrolyte. We also anticipate that materials could also be developed in which anions shift valence-band states into the band gap by a similar mechanism. These charge-switching states originate from interstitial and substitutional defects. We calculated the equilibrium electrochemical potentials at which these states are reduced and predicted the effect of the electrochemical operating conditions on their contribution to charge storage. Using the framework we have employed here for MnO_2 , computational materials screening can be employed to rapidly downselect and identify viable new pseudocapacitive materials, in line with efforts already in place to computationally identify materials for other electrochemical applications.

5.2 Concluding Remarks

Many technological advances have been driven by the discovery of new materials and defect properties. Unfortunately, material optimization by Edisonian or combinatorial methods can be both time and resource consuming. Although we have demonstrated the accurate prediction of materials properties and atomistic mechanisms using *ab initio* methods for two important applications in emerging technologies, much remains undiscovered in identifying new properties and the role of defects in materials. First-principles computations will continue to be an integral part of characterizing materials and defect properties, and in a number of areas theory has led experiment in understanding and guiding the development of these aspects of materials. More and more, proven computational methodologies are being implemented to predict, screen, and optimize materials at larger scales and faster rates. The future of computational materials and defect theory is promising and as it advances, so will it continue to enable the discovery of improved materials for the next generation of clean energy systems and advanced electronics, as well as enabling many other technologies yet to be developed that will improve and support our overall state of life.

Bibliography

- [1] W. Kohn and L. J. Sham, Physical Review 140 (1965) A1133.
- [2] P. Hohenberg and W. Kohn, Physical Review 136 (1964) B864.
- [3] E. Schrödinger, Physical Review 28 (1926) 1049.
- [4] J. Hafner, C. Wolverton, and G. Ceder, MRS bulletin 31 (2006) 659.
- [5] G. Hautier, A. Jain, and S. Ong, Journal of Materials Science 47 (2012) 7317.
- [6] H. Chen, G. Hautier, and G. Ceder, Journal of the American Chemical Society 134 (2012) 19619.
- [7] H. Chen, G. Hautier, A. Jain, C. Moore, B. Kang, R. Doe, L. Wu, Y. Zhu, Y. Tang, and G. Ceder, Chemistry of Materials 24 (2012) 2009.
- [8] J. Greeley, T. F. Jaramillo, J. Bonde, I. Chorkendorff, and J. K. Norskov, Nat Mater 5 (2006) 909.
- [9] L. Yu and A. Zunger, Physical Review Letters 108 (2012) 068701.
- [10] I. E. Castelli, D. D. Landis, K. S. Thygesen, S. Dahl, I. Chorkendorff, T. F. Jaramillo, and K. W. Jacobsen, Energy & Environmental Science 5 (2012) 9034.
- [11] I. E. Castelli, T. Olsen, S. Datta, D. D. Landis, S. Dahl, K. S. Thygesen, and K. W. Jacobsen, Energy & Environmental Science 5 (2012) 5814.
- [12] J. Lu, Z. Z. Fang, Y. J. Choi, and H. Y. Sohn, The Journal of Physical Chemistry C 111 (2007) 12129.
- [13] S. V. Alapati, J. K. Johnson, and D. S. Sholl, The Journal of Physical Chemistry B 110 (2006) 8769.
- [14] L.-C. Lin, A. H. Berger, R. L. Martin, J. Kim, J. A. Swisher, K. Jariwala, C. H. Rycroft, A. S. Bhown, M. W. Deem, M. Haranczyk, and B. Smit, Nat Mater 11 (2012) 633.
- [15] K. Yang, W. Setyawan, S. Wang, M. Buongiorno Nardelli, and S. Curtarolo, Nat Mater 11 (2012) 614.
- [16] S. Wang, Z. Wang, W. Setyawan, N. Mingo, and S. Curtarolo, Physical Review X 1 (2011) 021012.

- [17] S. B. Zhang and J. E. Northrup, Physical Review Letters 67 (1991) 2339.
- [18] C. G. Van de Walle and J. Neugebauer, Journal of Applied Physics 95 (2004) 3851.
- [19] J. B. Varley, H. Peelaers, A. Janotti, and C. G. Van de Walle, Journal of Physics-Condensed Matter 23 (2011)
- [20] S. Poykko, M. J. Puska, and R. M. Nieminen, Physical Review B 53 (1996) 3813.
- [21] T. Mattila and A. Zunger, Physical Review B 58 (1998) 1367.
- [22] K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, Physical Review B 30 (1984) 4734.
- [23] C. Franchini, R. Podloucky, J. Paier, M. Marsman, and G. Kresse, Physical Review B 75 (2007) 195128.
- [24] A. Alkauskas, P. Broqvist, and A. Pasquarello, physica status solidi (b) 248 (2011) 775.
- [25] G. Pacchioni, The Journal of Chemical Physics 128 (2008)
- [26] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Journal of Chemical Physics 118 (2003) 8207.
- [27] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Journal of Chemical Physics 124 (2006)
- [28] T. M. Henderson, B. G. Janesko, and G. E. Scuseria, The Journal of Chemical Physics 128 (2008)
- [29] M. Shishkin and G. Kresse, Physical Review B 74 (2006) 035101.
- [30] M. Shishkin and G. Kresse, Physical Review B 75 (2007) 235102.
- [31] L. DiCarlo, J. M. Chow, J. M. Gambetta, L. S. Bishop, B. R. Johnson, D. I. Schuster, J. Majer, A. Blais, L. Frunzio, S. M. Girvin, and R. J. Schoelkopf, Nature 460 (2009) 240.

- [32] E. Lucero, R. Barends, Y. Chen, J. Kelly, M. Mariantoni, A. Megrant, P. O/'Malley, D. Sank, A. Vainsencher, J. Wenner, T. White, Y. Yin, A. N. Cleland, and J. M. Martinis, Nat Phys 8 (2012) 719.
- [33] R. W. Simmonds, K. M. Lang, D. A. Hite, S. Nam, D. P. Pappas, and J. M. Martinis, Physical Review Letters 93 (2004) 077003.
- [34] J. M. Martinis, K. B. Cooper, R. McDermott, M. Steffen, M. Ansmann, K. D. Osborn, K. Cicak, S. Oh, D. P. Pappas, R. W. Simmonds, and C. C. Yu, Physical Review Letters 95 (2005) 210503.
- [35] H. Paik and K. D. Osborn, Applied Physics Letters 96 (2010)
- [36] T. Proslier, J. Zasadzinski, J. Moore, M. Pellin, J. Elam, L. Cooley, C. Antoine, J. Norem, and K. E. Gray, Applied Physics Letters 93 (2008)
- [37] D. S. Wisbey, J. Gao, M. R. Vissers, F. C. S. da Silva, J. S. Kline, L. Vale, and D. P. Pappas, Journal of Applied Physics 108 (2010)
- [38] P. w. Anderson, B. I. Halperin, and c. M. Varma, Philosophical Magazine 25 (1972) 1.
- [39] W. A. Phillips, Journal of Low Temperature Physics 7 (1972) 351.
- [40] W. A. Phillips, Reports on Progress in Physics 50 (1987) 1657.
- [41] H. M. Carruzzo, E. R. Grannan, and C. C. Yu, Physical Review B 50 (1994) 6685.
- [42] A. Burin, Journal of Low Temperature Physics 100 (1995) 309.
- [43] L. Faoro and L. B. Ioffe, Physical Review Letters 109 (2012) 157005.
- [44] R. C. Zeller and R. O. Pohl, Physical Review B 4 (1971) 2029.
- [45] M. v. Schickfus and S. Hunklinger, Journal of Physics C: Solid State Physics 9 (1976) L439.
- [46] B. Golding, M. v. Schickfus, S. Hunklinger, and K. Dransfeld, Physical Review Letters 43 (1979) 1817.
- [47] W. A. Phillips, Philosophical Magazine Part B 43 (1981) 747.
- [48] K. W. Hutt, W. A. Phillips, and R. J. Butcher, Journal of Physics: Condensed Matter 1 (1989) 4767.

- [49] M. J. A. Stoutimore, M. S. Khalil, C. J. Lobb, and K. D. Osborn, Applied Physics Letters 101 (2012)
- [50] J. R. Jameson, D. Ngo, C. Benko, J. P. McVittie, Y. Nishi, and B. A. Young, Journal of Non-Crystalline Solids 357 (2011) 2148.
- [51] M. S. Khalil, M. J. A. Stoutimore, S. Gladchenko, A. M. Holder, C. B. Musgrave, A. C. Kozen, G. Rubloff, Y. Q. Liu, R. G. Gordon, J. H. Yum, S. K. Banerjee, C. J. Lobb, and K. D. Osborn, Applied Physics Letters 103 (2013)
- [52] P. E. Blöchl, Physical Review B 50 (1994) 17953.
- [53] G. Kresse and J. Furthmüller, Computational Materials Science 6 (1996) 15.
- [54] G. Kresse and D. Joubert, Physical Review B 59 (1999) 1758.
- [55] M. Marsman, J. Paier, A. Stroppa, and G. Kresse, Journal of Physics-Condensed Matter 20 (2008)
- [56] M. Lucht, M. Lerche, H.-C. Wille, Y. V. Shvyd'ko, H. D. Ruter, E. Gerdau, and P. Becker, Journal of Applied Crystallography 36 (2003) 1075.
- [57] R. H. French, Journal of the American Ceramic Society 73 (1990) 477.
- [58] W. M. Haynes, CRC Handbook of Chemistry and Physics, 93rd Edition (CRC Handbook of Chemistry & Physics), CRC Press, 2012.
- [59] J. Ahn and J. W. Rabalais, Surface Science 388 (1997) 121.
- [60] E. A. Soares, M. A. Van Hove, C. F. Walters, and K. F. McCarty, Physical Review B 65 (2002)
- [61] P. J. Eng, T. P. Trainor, G. E. Brown Jr., G. A. Waychunas, M. Newville, S. R. Sutton, and M. L. Rivers, Science 288 (2000) 1029.
- [62] M. S. Khalil, F. C. Wellstood, and K. D. Osborn, Applied Superconductivity, IEEE Transactions on 21 (2011) 879.
- [63] G. Henkelman and H. Jónsson, The Journal of Chemical Physics 113 (2000) 9978.
- [64] R. Isnard and J. Gilchrist, Chemical Physics 52 (1980) 405.

- [65] G. Henkelman, A. Arnaldsson, and H. Jónsson, Computational Materials Science 36 (2006) 354.
- [66] E. Sanville, S. D. Kenny, R. Smith, and G. Henkelman, Journal of Computational Chemistry 28 (2007) 899.
- [67] S. P. Adiga, P. Zapol, and L. A. Curtiss, The Journal of Physical Chemistry C 111 (2007) 7422.
- [68] W. M. Hlaing Oo, S. Tabatabaei, M. D. McCluskey, J. B. Varley, A. Janotti, and C. G. Van de Walle, Physical Review B 82 (2010) 193201.
- [69] J. B. Varley, H. Peelaers, A. Janotti, and C. G. V. d. Walle, Journal of Physics: Condensed Matter 23 (2011) 334212.
- [70] J. R. Miller and P. Simon, Science 321 (2008) 651.
- [71] A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, and W. Van Schalkwijk, Nature Materials 4 (2005) 366.
- [72] C. Merlet, B. Rotenberg, P. A. Madden, P.-L. Taberna, P. Simon, Y. Gogotsi, and M. Salanne, Nature Materials 11 (2012) 306.
- [73] P. Simon and Y. Gogotsi, Nat Mater 7 (2008) 845.
- [74] R. Kotz and M. Carlen, Electrochimica Acta 45 (2000) 2483.
- [75] C. Xu, F. Kang, B. Li, and H. Du, Journal of Materials Research 25 (2010) 1421.
- [76] D. Bélanger, T. Brousse, and J. W. Long, Electrochemical Society Interface 17 (2008) 47.
- [77] V. Khomenko, E. Raymundo-Pinero, and F. Béguin, Journal of Power Sources 153 (2006) 183.
- [78] A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle, Physical Review B 61 (2000) 15019.
- [79] M. D. Radin and D. J. Siegel, Energy & Environmental Science 6 (2013) 2370.
- [80] A. M. Holder, K. D. Osborn, C. J. Lobb, and C. B. Musgrave, Physical Review Letters 111 (2013) 065901.

- [81] M. Toupin, T. Brousse, and D. Bélanger, Chemistry of Materials 16 (2004) 3184.
- [82] H. Y. Lee and J. B. Goodenough, Journal of Solid State Chemistry 144 (1999) 220.
- [83] S. Wen, J.-W. Lee, I.-H. Yeo, J. Park, and S.-i. Mho, Electrochimica Acta 50 (2004) 849.
- [84] S. C. Pang, M. A. Anderson, and T. W. Chapman, Journal of the Electrochemical Society 147 (2000) 444.
- [85] S.-F. Chin, S.-C. Pang, and M. A. Anderson, Journal of the Electrochemical Society 149 (2002) A379.
- [86] S.-L. Kuo and N.-L. Wu, Journal of the Electrochemical Society 153 (2006) A1317.
- [87] L. Mai, H. Li, Y. Zhao, L. Xu, X. Xu, Y. Luo, Z. Zhang, W. Ke, C. Niu, and Q. Zhang, Scientific reports 3 (2013)
- [88] S. W. Lee, J. Kim, S. Chen, P. T. Hammond, and Y. Shao-Horn, Acs Nano 4 (2010) 3889.
- [89] S. Devaraj and N. Munichandraiah, The Journal of Physical Chemistry C 112 (2008) 4406.
- [90] T. Brousse, M. Toupin, R. Dugas, L. Athouël, O. Crosnier, and D. Bélanger, Journal of the Electrochemical Society 153 (2006) A2171.
- [91] D. A. Tompsett and M. S. Islam, Chemistry of Materials 25 (2013) 2515.
- [92] D. A. Tompsett, S. C. Parker, P. G. Bruce, and M. S. Islam, Chemistry of Materials 25 (2013) 536.
- [93] T. Norby, MRS bulletin 34 (2009) 923.
- [94] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters 77 (1996) 3865.
- [95] B. L. Zhu, L. Lv, and X. J. Wang, Key Engineering Materials 492 (2012) 264.
- [96] D. B. Rogers, R. D. Shannon, A. W. Sleight, and J. L. Gillson, Inorganic Chemistry 8 (1969) 841.

- [97] M. Suzuki and I. S. Suzuki, arXiv preprint arXiv:1001.1539 (2010)
- [98] S. Fritsch and A. Navrotsky, Journal of the American Ceramic Society 79 (1996) 1761.
- [99] C. Daniel and J. O. Besenhard, Handbook of battery materials, John Wiley & Sons, 2013.
- [100] D. M. Sherman, Geochimica et Cosmochimica Acta 69 (2005) 3249.
- [101] N. Sakai, Y. Ebina, K. Takada, and T. Sasaki, The Journal of Physical Chemistry B 109 (2005) 9651.
- [102] S. Lany and A. Zunger, Physical Review B 78 (2008) 235104.
- [103] A. J. Bard and L. R. Faulkner, Electrochemical methods: fundamentals and applications, Wiley New York, 2000.
- [104] A. A. Isse and A. Gennaro, The Journal of Physical Chemistry B 114 (2010) 7894.
- [105] V. Tripkovic, M. E. Björketun, E. Skúlason, and J. Rossmeisl, Physical Review B 84 (2011) 115452.
- [106] P. Ragupathy, H. N. Vasan, and N. Munichandraiah, Journal of the Electrochemical Society 155 (2008) A34.
- [107] C. Fall, N. Binggeli, and A. Baldereschi, Journal of Physics: Condensed Matter 11 (1999) 2689.
- [108] R. Eastment and C. Mee, Journal of Physics F: Metal Physics 3 (1973) 1738.
- [109] H.-Y. Su, Y. Gorlin, I. C. Man, F. Calle-Vallejo, J. K. Nørskov, T. F. Jaramillo, and J. Rossmeisl, Physical Chemistry Chemical Physics 14 (2012) 14010.
- [110] B. Prélot, C. Poinsignon, F. Thomas, E. Schouller, and F. Villiéras, Journal of colloid and interface science 257 (2003) 77.
- [111] W.-f. Tan, S.-j. Lu, F. Liu, X.-h. Feng, J.-z. He, and L. K. Koopal, Soil Science 173 (2008) 277.
- [112] F. Ataherian and N.-L. Wu, Journal of the Electrochemical Society 158 (2011) A422.

- [113] F. Ataherian, K.-T. Lee, and N.-L. Wu, Electrochimica Acta 55 (2010) 7429.
- [114] P. Ruetschi, Journal of the Electrochemical Society 131 (1984) 2737.
- [115] C.-C. Ji, M.-W. Xu, S.-J. Bao, C.-J. Cai, R.-Y. Wang, and D.-Z. Jia, Journal of Solid State Electrochemistry 17 (2013) 1357.
- [116] M. Toupin, T. Brousse, and D. Bélanger, Chemistry of Materials 14 (2002) 3946.
- [117] A. l. Boisset, L. Athouel, J. Jacquemin, P. Porion, T. Brousse, and M. r. m. Anouti, The Journal of Physical Chemistry C 117 (2013) 7408.
- [118] B. Conway, Electrochemical supercapacitors: scientific fundamentals and technological applications, Kluwer Academic/Plenum: New York, 1999.
- [119] T. Bak, J. Nowotny, M. Rekas, and C. Sorrell, International journal of hydrogen energy 27 (2002) 991.
- [120] J. K. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen, Nature chemistry 1 (2009) 37.
- [121] S. Curtarolo, G. L. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, Nature Materials 12 (2013) 191.
- [122] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, and G. Ceder, APL Materials 1 (2013) 011002.